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SURVEY REPORTS ON ATMOSPHERIC EMISSIONS FROM THE PETROCHEMICAL INDUSTRY. VOLUME I

J. W. Pervier, et al

Air Products and Chemicals, Incorporated

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SURVEY REPORTS ON ATMOSPHERIC EMISSIONS FROM THE PETROCHEMICAL INDUSTRY

VOLUME I

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16. ABSTRACT

This document is one of a series of four volumes prepared for the Environmental Protection Agency (EPA) to assist it in determining the significance of air pollution from the petrochemical industry. A total of 33 distinctly different processes which are used to produce 27 petrochemicals have been surveyed, and the results are reported in four volumes numbered EPA-450/3-73-005-a, -b, -c, and -d.

This volume covers the following processes: acetaldehyde via ethylene, acetaldehyde via ethanol, acetic acid via methanol, acetic acid via butane, acetic acid via acetaldehyde, acetic anhydride, adipic acid, adiponitrile via butadiene, and adiponitrile via adipic acid. For each process the report includes a process description, a process emission inventory, a catalog of emission control equipment, a list of producers, and an evaluation of the significance of the air pollution from the process. Also included is a summary table of emissions to the atmosphere from all the processes studied.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Acetic Anhydride	Petrochemical Industry	7A
Carbon Monoxide	Adipic Acid		7B
Hydrocarbons	Adiponitrile	Particulates	7C
Nitrogen Dioxide			13B
Sulfur Dioxide			13H
Acetaldehyde			
Acetic Acid			

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PETROCHEMICAL AIR POLLUTION STUDY

INTRODUCTION TO SERIES

This document is one of a series of four volumes prepared for the Environmental Protection Agency (EPA) to assist it in determining the significance of air pollution from the petrochemical industry.

A total of 33 distinctly different processes which are used to produce 27 petrochemicals have been surveyed, and the results are reported in these four volumes numbered EPA 450/3-73-005-a, -b, -c, and -d. The Tables of Contents of these reports list the processes that have been surveyed.

Those processes which have a significant impact on air quality are being studied in more detail by EPA. These in-depth studies will be published separately in a series of volumes entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006-a, -b, -c, etc.) At the time of this writing, a total of seven petrochemicals produced by 11 distinctly different processes has been selected for this type of study. Three of these processes, used to produce two chemicals (polyethylene and formaldehyde), were selected because the survey reports indicated further study was warranted. The other five chemicals (carbon black, acrylonitrile, ethylene dichloride, phthalic anhydride and ethylene oxide) were selected on the basis of expert knowledge of the pollution potential of their production processes. One or more volumes in the report series will be devoted to each of these chemicals.

ACKNOWLEDGEMENTS

Survey and study work such as that described in this report have value only to the extent of the value of the imput data. Without the fullest cooperation of the companies involved in producing the petrochemicals that have been studied, this report would not have been possible. Air Products wishes to acknowledge this cooperation by commending:

The U. S. Petrochemical Industy
Member Companies of the Industry
The Manufacturing Chemists Association

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*Fifteen highest ranks from Table I.

NOTE: There are numerous tables and figures in the Survey Reports that are included in the appendicies of this report. These tables and figures are separately listed in each appendix.

SUMMARY

A study of air pollution as caused by the petrochemical industry has been undertaken in order to provide data that the Environmental Protection Agency can use in the fulfillment of their obligations under the terms of the Clean Air Amendments of 1970. The scope of the study includes most petrochemicals which fall into one or more of the classifications of (a) large production, (b) high growth rate, and (c) significant air pollution. The processes for the production of each of these selected chemicals have been studied and the emissions from each tabulated on the basis of data from and Industry Questionnaire. A survey report prepared for each process provides a method for ranking the significance of the air pollution from these processes. In-depth studies on those processes which are considered to be among the more significant polluters either have been or will be provided.

To date, drafts of in-depth studies on seven processes have been submitted. In addition, two further processes have been selected for in-depth study and work on these is in progress. All of these in-depth studies will be separately reported under Report Number EPA-450/3-73-006 a, b, c, etc.

A total of 33 Survey Reports have been completed and are reported here, or in one of the other three volumes of this report series.

I. Introduction

A study has been undertaken to obtain information about selected production processes that are practiced in the Petrochemical Industry. The objective of the study is to provide data that are necessary to support the Clean Air Ammendments of 1970.

The information sought includes industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions and descriptions of emission control devices currently in use. The principal source for these data was an industry questionnaire but it was supplemented by plant visits, literature searches, in-house background knowledge and direct support from the Manufacturing Chemists Association.

A method for rating the significance of air emissions was established and is used to rank the processes as they are studied. The goal of the ranking technique is to aid in the selection of candidates for in-depth study. These studies go beyond the types of information outlined above and include technical and economic information on "best systems" of emission reduction, the economic impact of these systems, deficiencies in petrochemical pollution control technology and potential research and development programs to overcome these deficiencies. These studies also recommend specific plants for source testing and present suggested checklists for inspectors.

This final report presents a description of the industry surveys that have been completed, as well as a status summary of work on the in-depth studies.

The Appendicies of this report include each of the 33 Survey Reports that were prepared during the course of the study.

II. Discussion

A. Petrochemicals to be Studied

There are more than 200 different petrochemicals in current production in the United States. Many of these are produced by two or more processes that are substantially different both with respect to process techniques and nature of air emissions. Although it may eventually become necessary to study all of these, it is obvious that the immediate need is to study the largest tonnage, fastest growth processes that produce the most pollution.

Recognizing this immediate need, a committee of Air Products' employees and consultants reviewed the entire list of chemicals and prepared a list of thirty chemicals which were recommended for primary consideration in the study and an additional list of fourteen chemicals that should receive secondary consideration. Since this was only a qualitative evaluation it was modified slightly as additional information was received and after consultation with the Environmental Protection Agency (EPA).

The final modified list of chemicals to be studied included all but three from the original primary recommendations. In addition, four chemicals were added and one was broken into two categories (namely low and high density polyethylene) because of distinct differences in the nature of the final products. This resulted in thirty-two chemicals for study and fourty one processes which are sufficiently different to warrant separate consideration. Hence, the following list of petrochemicals is the subject of this study.

Acetaldehyde (2 processes)
Acetic Acid (3 processes)
Acetic Anhydride
Acrylonitrile
Adipic Acid
Adiponitrile (2 processes)
Carbon Black
Carbon Disulfide
Cyclohexanone
Ethylene
Ethylene Dichloride (2 processes)
Ethylene Oxide (2 processes)
Formaldehyde (2 processes)
Glycerol
Hydrogen Cyanide
Maleic Anhydride
Nylon 6
Nylon 6,6
"Oxo" Alcohols and Aldehydes
Phenol
Phthalic Anhydride (2 processes)
Polyethylene (high density)
Polyethylene (low density)
Polypropylene
Polystyrene
Polyvinyl Chloride
Styrene
Styrene - Butadiene Rubber
Terephthalic Acid (1)
Toluene Di-isocyanate (2)
Vinyl Acetate (2 processes)
Vinyl Chloride

(1) Includes dimethyl terephthalate.
(2) Includes methylenediphenyl and polymethylene polyphenyl isocyanates.

B. Preliminary Investigations

Immediately upon completion of the preliminary study lists, a literature review was begun on those chemicals which were considered likely candidates for study. The purpose of the review was to prepare an informal "Process Portfolio" for each chemical. Included in the portfolio are data concerning processes for producing the chemical, estimates of growth in production, estimates of production costs, names, locations and published capacities of producers, approximations of overall plant material balances and any available data on emissions or their control as related to the specific process.

The fundamental purpose of these literature reviews was to obtain background knowledge to supplement what was ultimately to be learned from completed Industry Questionnaires. A second and very important purpose was to determine plant locations and names of companies producing each chemical. This information was then used to contact responsible individuals in each organization (usually by telephone) to obtain the name and address of the person to whom the Industry Questionnaire should be directed. It is believed that this approach greatly expedited the completion of questionnaires. The mailing list that was used is included as Appendix I of this report.

C. Industry Questionnaire

Soon after the initiation of the petrochemical pollution study, a draft questionnaire was submitted by Air Products to the Environmental Protection Agency. It had been decided that completion of this questionnaire by industry would provide much of the information necessary to the performance of the study. The nature and format of each question was reviewed by EPA engineers and discussed with Air Products engineers to arrive at a modified version of the originally proposed questionnaire.

The modified questionnaire was then submitted to and discussed with an Industry Advisory Committee (IAC) to obtain a final version for submission to the Office of Management and Budget (OMB) for final approval, as required prior to any U. S. Government survey of national industries. The following listed organizations, in addition to the EPA and Air Products, were represented at the IAC meeting:

Trade Associations

Industrial Gas Cleaning Institute
Manufacturing Chemists Association

Petrochemical Producers

B. F. Goodrich Chemical Company
E. I. duPont deNemours and Company
Exxon Chemical Company
FMC Corporation
Monsanto Company
Northern Petrochemical Company
Shell Chemical Company
Tenneco Chemicals, Inc.
Union Carbide Corporation

Manufacturers of Pollution Control Devices

John Zink Company
UOP Air Correction Division

State Pollution Control Departments

New Jersey
Texas

The questionnaire, along with a detailed instruction sheet and an example questionnaire (which had been completed by Air Products for a fictitious process that was "invented" for this purpose) were submitted to the OMB for approval. In due course, approval was received and OMB Approval Number 158-S-72019 was assigned to the questionnaire. Copies of the approved instruction sheet, example questionnaire are included as Appendix II of this report.

The questionnaires were mailed in accordance with the mailing list already discussed and with a cover letter that had been prepared and signed by the EPA Project Officer. The cover letter was typed in a manner that permitted the insertion of the name and address of the receipient at the top of the first page and the name of the process, the plant location and an expected return date at the bottom of the first page. A copy of this letter of transmittal is also included in Appendix II.

Understandably, because of the dynamic nature of the petrochemical industry, about 10 percent of the questionnaires were directed to plants which were no longer in operation, were still under construction, were out-of-date processes or were too small to be considered as typical. This did not present a serious problem in most cases because (a) 100 percent of the plants were not surveyed and (b) the project timing permitted a second mailing when necessary. Appendix III tabulates the number of questionnaires incorporated into each study.

One questionnaire problem that has not been resolved is confidentiality. Some respondents omitted information that they consider to be proprietary. Others followed instructions by giving the data but then marked the sheet (or questionnaire) "Confidential". The EPA is presently trying to resolve this problem, but until they do the data will be unavailable for inclusion in any Air Products' reports.

D. Screening Studies

Completed questionnaires were returned by the various respondents to the EPA's Project Officer, Mr. L. B. Evans. After reviewing them for confidentiality, he forwarded the non-confidential data to Air Products. These data form the basis for what has been named a "Survey Report". The purpose of the survey reports being to screen the various petrochemical processes into the "more" and "less - significantly polluting processes". These reports are included as appendicies to this report.

Obviously, significance of pollution is a term which is difficult if not impossible to define because value judgements are involved. Recognizing this difficulty, a quantitative method for calculating a Significant Emission Index (SEI) was developed. This procedure is discussed and illustrated in Appendix IV of this report. Each survey report includes the calculation of an SEI for the petrochemical that is the subject of the report. These SEI's have been incorporated into the Emissions Summary Table that constitutes part of this report. This table can be used as an aid when establishing priorities in the work required to set standards for emission controls on new stationary sources of air pollution in accordance with the terms of the Clean Air Amendments of 1970.

The completed survey reports constitute a preliminary data bank on each of the processes being studied. In addition to the SEI calculation, each report includes a general introductory discussion of the process, a process description (including chemical reactions), a simplified process (Block) flow diagram, as well as heat and material balances. More pertinent to the air pollution study, each report lists and discusses the sources of air emissions (including odors and fugitive emissions) and the types of air pollution control equipment employed. In tabular form, each reports summarizes the emission data (amount, composition, temperature, and frequency); the sampling and analytical techniques; stack numbers and dimensions; and emission control device data (types, sizes, capital and operating costs and efficiencies).

Calculation of efficiency on a pollution control device is not necessarily a simple and straight-forward procedure. Consequently, two rating techniques were established for each type of device, as follows:

1. For flares, incinerators, and boilers a Completeness of Combustion Rating (CCR) and Significance of Emission Reduction Rating (SERR) are proposed.

2. For scrubbers and dust removal equipment, a Specific Pollutant Efficiency (SE) and a SERR are proposed.

The bases for these ratings and example calculations are included in Appendix V of this report.

E. In-Depth Studies

The original performance concept was to select a number of petrochemical processes as "significant polluters", on the basis of data contained in completed questionnaires. These processes were then to be studied "in-depth". However, the overall time schedule was such that the EPA requested an initial selection of three processes on the basis that they would probably turn out to be "significant polluters". The processes selected in this manner were:

1. The Furance Process for producing Carbon Black.

2. The Sohio Process for producing Acrylonitrile.

3. The Oxychlorination Process for producing 1,2 Dichloroethane (Ethylene Dichloride) from Ethylene.

In order to obtain data on these processes, the operators and/or licensors of each were approached directly by Air Products' personnel. This, of course, was a slow and tedious method of data collection because mass mailing techniques could not be used, nor could the request for data be identified as an "Official EPA Requirement". Yet, by the time that OMB approval was given for use of the Industry Questionnaire, a substantial volume of data pertaining to each process had already been received. The value of this procedure is indicated by the fact that first drafts of these three reports had already been submitted to the EPA, and reviewed by the Industry Advisory Committee, prior to the completion of many of the survey reports.

In addition, because of timing requirements, the EPA decided that three additional processes be "nominated" for in-depth study. The chemicals involved are phthalic anhydride, formaldehyde and ethylene oxide. Work on these indicated a need for four additional in-depth studies as follows:

1. Air Oxidation of Ortho-Xylene to produce Phthalic Anhydride.
2. Air Oxidation of Methanol in a Methanol Rich Process to produce Formaldehyde over a Silver Catalyst.
3. Air Oxidation of Methanol in a Methanol-lean Process to produce Formaldehyde over an Iron Oxide Catalyst.
4. Direct Oxidation of Ethylene to produce Ethylene Oxide.

Drafts of these have been submitted to the EPA and reviewed by the Industry Advisory Committee. The phthalic anhydride report also includes a section on production from naphthalene by air oxidation, a process which is considered to be a significant polluter in today's environment but without significant growth potential.

These seven in-depth studies will be separately issued in final report form, under Report Number EPA-450/3-73-006 a, b, c, etc.

An in-depth study, besides containing all the elements of the screening studies, delves into questions such as "What are the best demonstrated systems for emission reduction?", "What is the economic impact of emission control on the industry involved?", "What deficiencies exist in sampling, analytical and control technology for the industry involved?".

In striving to obtain answers to these questions, the reports include data on the cost effectiveness of the various pollution control techniques source testing recommendations, industry growth projections, inspection procedures and checklists, model plant studies of the processes and descriptions of research and development programs that could lead to emission reductions.

Much of the information required to answer these questions came from the completed Industry Questionnaires and the Process Portfolios. However, the depth of understanding that is required in the preparation of such a document can only be obtained through direct contact with the companies that are involved in the operation of the processes being studied. Three methods for making this contact were available to Air Products. The first two are self-evident, as follows: Each questionnaire contains the name, address and telephone number of an individual who can provide additional information. By speaking with him, further insight was obtained into the pollution control problems that are specific to the process being studied; or through him, a visit to an operating plant was sometimes arranged, thus achieving a degree of first hand knowledge.

However, it was felt that these two techniques might fall short of the level of knowledge desired. Thus, a third, and unique procedure was arranged. The Manufacturing Chemists Association (MCA) set up, through its Air Quality Committee (AQC), a Coordinating Technical Group (CTG) for each in-depth process. The role of each CTG was to:

1. Assist in the obtaining of answers to specific questions.
2. Provide a review and commentary (without veto power) on drafts of reports.

The AQC named one committee member to provide liaison. In several cases, he is also one of the industry's specialists for the process in question. If not, one other individual was named to provide CTG leadership. Coordination of CTG activities was provided by Mr. Howard Guest of Union Carbide Corporation who is also on the EPA's Industry Advisory Committee as the MCA Representative. CTG leadership is as follows:

Chemical	AQC Member	Other
Carbon Black	C. B. Beck Cabot Corporation	None
Acrylonitrile	W. R. Chalker Du Pont	R. E. Farrell Sohio
Formaldehyde	W. B. Barton Borden	None
Ethylene Dichloride	W. F. Bixby B. F. Goodrich	None
Phthalic Anhydride	E. P. Wheeler Monsanto	Paul Hodges Monsanto
Ethylene Oxide	H. R. Guest Union Carbide	H. D. Coombs Union Carbide

F. Current Status

Survey Reports on each of the 33 processes that were selected for this type of study have been completed, following review of the drafts by both the EPA and the Petrochemical Industry. These reports constitute the subject matter of this report.

In-depth studies of the seven processes mentioned above have been completed in draft form, submitted to the EPA for initial review, discussed in a public meeting with the Industry Advisory Committee and re-submitted to the EPA in revised form. They are currently receiving final EPA review and will be issued as final reports, following that review.

The EPA has now selected two additional processes for in-depth study and work on these is currently in progress. They are:

1. High Density Polyethylene via the Low and Intermediate Pressure Polymerization of Ethylene.
2. Low Density Polyethylene via the High Pressure Polymerization of Ethylene.

III. Results

The nature of this project is such that it is not possible to report any "results" in accordance with the usual meaning of the word. Obviously, the results are the Survey Reports and In-Depth Studies that have been prepared. However, a tabulation of the emission data collected in the study and summarized in each of these reports will be useful to the EPA in the selection of those processes which will be either studied in-depth at some future date, or selected for the preparation of new source standards. Such a tabulation, entitled "Emissions Summary Table", is attached.

IV. Conclusions

As was stated above under "Results", the conclusions reached are specific to each study and, hence, are given in the individual reports. Ultimately, some conclusions are reachable relative to decisions on processes which require future in-depth studies or processes which warrant the promulgation of new source standards.

A firm basis for selecting these processes is difficult to achieve, but the data contained in the Emissions Summary Table can be of value in setting a basis, or selecting processes.

It is imperative, when using the table, to be aware of the following facts.

1. The data for some processes are based on 100 percent survey of the industry, while others are based on less than 100 percent with some as few as a single questionnaire.
2. Some of the reported data are based on stack sampling, others on continuous monitoring and still others on the "best estimate" by the person responsible for the questionnaire.
3. Air Products attempted to use sound engineering judgement in obtaining emission factors, industry capacities and growth projections. However, other engineering firms, using the same degree of diligence would undoubtedly arrive at somewhat different final values.

Thus, the tabulation should be used as a guide but not as a rigorous comparison of process emissions.

Furthermore, data on toxicity of emissions, odors and persistence of emitted compounds are not included in the tabulation. In addition, great care must be used when evaluating the weighted emission rates because of the wide range in noxiousness of the materials lumped together in the two most heavily weighted categories. For example, "hydrocarbons" includes both ethane and formaldehyde and "particulates" includes both phthalic anhydride and the permanent hardness of incinerated water.

Bearing all of these qualifications in mind, several "top 15" rankings of processes can be made, as in Tables II through V. Obviously, one of these tables could be used to select the more significant polluters directly. Of course, other rankings could be made, such as leading emitters of NO_x or particulates, etc. Using these four tables, however, one analysis might be that the number of times a process appears in these tables is a measure of its pollution significance, or in summary:

Appear in 4 Tables

Carbon Black
Low Density Polyethylene
High Density Polyethylene
Cyclohexanone
Polypropylene
Polyvinyl Chloride
Ethylene Oxide

Appear in 3 Tables

Acrylonitrile
Adiponitrile (Butadiene)
Ethylene Dichloride (Oxychlorination)
Dimethyl Terephthalate
Ethylene Dichloride (Direct)
Ethylene

Appear in 2 Tables

Maleic Anhydride
Isocyanates
Phenol
Formaldehyde (Silver)

Appear in 1 Table

Phthalic Anhydride
Formaldehyde (Iron Oxide)
Polystyrene
Nylon 6
Nylon 6,6
Vinyl Chloride

Thus, on this basis and in retrospect, it could be concluded that four of the selected in-depth studies (carbon black, ethylene oxide, and both low and high density polyethylene) were justified but that three of them (phthalic anhydride and both formaldehyde processes) were of lesser importance.

On the same basis, seven processes should be considered for future in-depth studies, namely:

Cyclohexanone
Polypropylene
Polyvinyl Chloride
Adiponitrile (Butadiene Process)
Dimethyl Terephthalate (and TPA)
Ethylene Dichloride (Direct)
Ethylene

Obviously, many alternative bases could be established. It is not the function of this report to select a basis for initiating future studies because the priorities of the EPA are unknown. The most apparent of these bases are the ones suggested by Tables II through V, namely the worst total polluters, the worst polluters on a weighted basis, the greatest increase in pollution (total or weighted) or the largest numbers of new plants. In addition, noxiousness of the emissions (photo-chemical reactivity, toxicity, odor, persistence) could be considered in making a selection.

TABLE I
EMISSIONS SUMMARY

Page 1 of 3

ESTIMATED (1) CURRENT AIR EMISSIONS, MM LBS./YEAR

	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5)
Acetaldehyde via Ethylene	1.1	0	0	0	0	1.1	86
via Ethanol	0	0	0	0	27	27	27
Acetic Acid via Methanol	0	0	0.01	0	0	0.01	1
via Butane	40	0	0.04	0	14	54	3,215
via Acetaldehyde	6.1	0	0	0	1.3	7.4	490
Acetic Anhydride via Acetic Acid	3.1	0	0	0	5.5	8.6	253
Acrylonitrile (9)	183	0	5.5	0	196	385	15,000
Adipic Acid	0	0.2	29.6	0	0.14	30	1,190
Adiponitrile via Butadiene	11.2	4.7	50.5	0	0	66.4	3,200
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	156	8.1	6.9	21.6	3,870	4,060	17,544
Carbon Disulfide	0.15	0.3	0.1	4.5	0	5.1	120
Cyclohexanone	70	0	0	0	77.5	148	5,700
Dimethyl Terephthalate (+TPA)	91	1.4	0.1	1.0	53	146.5	7,460
Ethylene	15	0.2	0.2	2.0	0.2	17.6	1,240
Ethylene Dichloride via Oxychlorination	95.1	0.4	0	0	21.8	117.3	7,650
via Direct Chlorination	29	0	0	0	0	29	2,300
Ethylene Oxide	85.8	0	0.3	0.1	0	86.2	6,880
Formaldehyde via Silver Catalyst	23.8	0	0	0	107.2	131	1,955
via Iron Oxide Catalyst	25.7	0	0	0	24.9	50.6	2,070
Glycerol via Epichlorohydrin	16	0	0	0	0	16	1,280
Hydrogen Cyanide Direct Process	0.5	0	0.41	0	0	0.91	56
Isocyanates	1.3	0.8	0	0.02	86	88	231
Maleic Anhydride	34	0	0	0	260	294	2,950
Nylon 6	0	1.5	0	0	0	1.5	90
Nylon 6,6	0	5.5	0	0	0	5.5	330
Oxo Process	5.25	0.01	0.07	0	19.5	24.8	440
Phenol	24.3	0	0	0	0	24.3	1,940
Phthalic Anhydride via O-Xylene	0.1	5.1	0.3	2.6	43.6	51.7	422
via Naphthalene	0	1.9	0	0	45	47	160
High Density Polyethylene	79	2.3	0	0	0	81.3	6,400
Low Density Polyethylene	75	1.4	0	0	0	76.4	6,100
Polypropylene	37.5	0.1	0	0	0	37.6	2,950
Polystyrene	20	0.4	0	1.2	0	21.6	1,650
Polyvinyl Chloride	62	12	0	0	0	74	5,700
Styrene	4.3	0.07	0.14	0	0	4.5	355
Styrene-Butadiene Rubber	9.4	1.6	0	0.9	0	12	870
Vinyl Acetate via Acetylene	5.3	0	0	0	0	5.3	425
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	17.6	0.6	0	0	0	18.2	1,460
Totals	1,227.6	49.1	94.2	33.9	4,852.6	6,225.9 (7)	110,220 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) Emissions based on what is now an obsolete catalyst. See Report No. EPA-450/3-73-006 b for up-to-date information.

TABLE I
EMISSION SUMMARY

ESTIMATED ADDITIONAL (2) AIR EMISSIONS IN 1980, MM LBS./YEAR

	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5,6)
Acetaldehyde via Ethylene	1.2	0	0	0	0	1.2	96
via Ethanol	0	0	0	0	0	0	0
Acetic Acid via Methanol	0	0	0.04	0	0	0.04	2
via Butane	0	0	0	0	0	0	0
via Acetaldehyde	12.2	0	0	0	2.5	14.7	980
Acetic Anhydride via Acetic Acid	0.73	0	0	0	1.42	2.15	60
Acrylonitrile (9)	284	0	8.5	0	304	596	23,000
Adipic Acid	0	0.14	19.3	0	0.09	19.5	779
Adiponitrile via Butadiene	10.5	4.4	47.5	0	0	62.4	3,010
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	64	3.3	2.8	8.9	1,590	1,670	7,200
Carbon Disulfide	0.04	0.07	0.03	1.1	0	1.24	30
Cyclohexanone	77.2	0	0	0	85.1	162	6,260
Dimethyl Terephthalate (+TPA)	73.8	1.1	0.07	0.84	42.9	118.7	6,040
Ethylene	14.8	0.2	0.2	61.5	0.2	77	2,430
Ethylene Dichloride via Oxychlorination	110	0.5	0	0	25	136	5,800
via Direct Chlorination	34.2	0	0	0	0	34.2	2,740
Ethylene Oxide	32.8	0	0.15	0.05	0	33	2,650
Formaldehyde via Silver Catalyst	14.8	0	0	0	66.7	81.5	1,250
via Iron Oxide Catalyst	17.6	0	0	0	17.0	34.6	1,445
Glycerol via Epichlorohydrin	8.9	0	0	0	0	8.9	700
Hydrogen Cyanide Direct Process	0	0	0	0	0	0	0
Isocyanates	1.2	0.7	0	0.02	85	87	225
Maleic Anhydride	31	0	0	0	241	272	2,720
Nylon 6	0	3.2	0	0	0	3.2	194
Nylon 6,6	0	5.3	0	0	0	5.3	318
Oxo Process	3.86	0.01	0.05	0	14.3	18.2	325
Phenol	21.3	0	0	0	0	21.3	1,704
Phthalic Anhydride via O-Xylene	0.3	13.2	0.8	6.8	113	134	1,100
via Naphthalene	0	0	0	0	0	0	0
High Density Polyethylene	210	6.2	0	0	0	216	17,200
Low Density Polyethylene	262	5	0	0	0	267	21,300
Polypropylene	152	0.5	0	0	0	152.5	12,190
Polystyrene	20	0.34	0	1.13	0	21.47	1,640
Polyvinyl Chloride	53	10	0	0	0	63	4,840
Styrene	3.1	0.05	0.1	0	0	3.25	225
Styrene-Butadiene Rubber	1.85	0.31	0	0.18	0	2.34	170
Vinyl Acetate via Acetylene	4.5	0	0	0	0	4.5	360
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	26.3	0.9	0	0	0	27.2	2,170
Totals	1,547.2	55.9	79.5	80.5	2,588	4,351.9	134,213 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 40, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down duw to rounding.
(9) See sheet 1 of 3.

TABLE I
EMISSIONS SUMMARY

Page 3 of 3

	Emissions (2), MM Lbs./Year		Estimated Number of New Plants (1973 - 1980)	Total Estimated Capacity MM Lbs./Year	
	Total by 1980	Total Weighted (5) by 1980		Current	By 1980
Acetaldehyde via Ethylene	2.3	182	6	1,160	2,460
via Ethanol	27	27	0	966	966
Acetic Acid via Methanol	0.05	3	4	400	1,800
via Butane	54	3,215	0	1,020	500
via Acetaldehyde	22	1,470	3	875	2,015
Acetic Anhydride via Acetic Acid	10.8	313	3	1,705	2,100
Acrylonitrile (9)	980	38,000	5	1,165	3,700 (8)
Adipic Acid	50	1,970	7	1,430	2,200
Adiponitrile via Butadiene	128.8	6,210	4	435	845
via Adipic Acid	1.1	60	3	280	550
Carbon Black	5,730	24,740	13	3,000	5,000 (8)
Carbon Disulfide	6.3	150	2	871	1,100
Cyclohexanone	310	11,960	10	1,800	3,600
Dimethyl Terephthalate (+TPA)	265	13,500	8	2,865	5,900
Ethylene	94	3,670	21	22,295	40,000
Ethylene Dichloride via Oxychlorination	253	16,450	8	4,450	8,250 (8)
via Direct Chlorination	63	5,040	10	5,593	11,540
Ethylene Oxide	120	9,530	15	4,191	6,800 (8)
Formaldehyde via Silver Catalyst	212.5	3,205	40	5,914	9,000
via Iron Oxide Catalyst	85	3,515	12	1,729	3,520 (8)
Glycerol via Epichlorohydrin	25	2,000	1	245	380
Hydrogen Cyanide Direct Process	0.5 (10)	28 (10)	0	412	202
Isocyanates	175	456	10	1,088	2,120
Maleic Anhydride	566	5,670	6	359	720
Nylon 6	4.7	284	10	486	1,500
Nylon 6,6	10.8	650	10	1,523	3,000
Oxo Process	43	765	6	1,727	3,000
Phenol	46	3,640	11	2,363	4,200
Phthalic Anhydride via O-Xylene	186	1,522	6	720	1,800 (8)
via Naphthalene	47	160	0	603	528
High Density Polyethylene	297	23,600	31	2,315	8,500
Low Density Polyethylene	343	27,400	41	5,269	21,100
Polypropylene	190	15,140	32	1,160	5,800
Polystyrene	43	3,290	23	3,500	6,700
Polyvinyl Chloride	137	10,540	25	4,375	8,000
Styrene	7.4	610	9	5,953	10,000
Styrene-Butadiene Rubber	14	1,040	4	4,464	5,230
Vinyl Acetate via Acetylene	9.8	785	1	206	356
via Ethylene	TR	TR	4	1,280	2,200
Vinyl Chloride	45	3,630	10	5,400	13,000
Totals	10,605 (7)	244,420 (7)			

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(8) By 1985.
(9) See sheet 1 of 3
(10) Due to anticipated future shut down of marginal plants.

TABLE II

TOTAL ANNUAL EMISSIONS, ALL "POLLUTANTS", BY 1980 (MM LBS./YR.)*	
Carbon Black	5,730
Acrylonitrile	980
Maleic Anhydride	566
Low Density Polyethylene	343
Cyclohexanone	310
High Density Polyethylene	297
Dimethyl Terephthalate	265
Ethylene Dichloride	253
Phthalic Anhydride (Total)	233
Formaldehyde (Silver)	212
Polypropylene	190
Isocyanates	175
Polyvinyl Chloride	137
Adiponitrile (Butadiene Process)	129
Ethylene Oxide	120

*Fifteen highest numbers, as summarized in Table I, for this category.

TABLE IV

SIGNIFICANT EMISSION INDEX*

Acrylonitrile	23,000
Low Density Polyethylene	21,300
High Density Polyethylene	17,200
Polypropylene	12,190
Ethylene Dichloride (Oxychlorination)	8,800
Carbon Black	7,200
Cyclohexanone	6,260
Dimethyl Terephthalate	6,040
Polyvinyl Chloride	4,840
Adiponitrile (Butadiene)	3,010
Ethylene Dichloride (Direct)	2,740
Maleic Anhydride	2,720
Ethylene Oxide	2,650
Ethylene	2,430
Vinyl Chloride	2,170

*Fifteen higest numbers, as summarized in Table I, for this category.

TABLE V

NUMBER OF NEW PLANTS (1973-1980)*

Low Density Polyethylene	41
Formaldehyde (Silver)	40
Polypropylene	32
High Density Polyethylene	31
Polyvinyl Chloride	25
Polystyrene	23
Ethylene	21
Ethylene Oxide	15
Carbon Black	13
Formaldehyde (Iron Oxide)	12
Phenol	11
Cyclohexanone	10
Isocyanates	10
Nylon 6	10
Nylon 6,6	10
Ethylene Dichloride (Direct)	10

*Fifteen highest numbers, as summarized in Table I, for this category.

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I. Introduction

Acetaldehyde, CH_3CHO, is a mobile, colorless, inflammable liquid with a pungent, choking odor. It was first noticed by Scheele in 1774 and recognized as a new compound by Foucroy and Vaughelin in 1880.

Most acetaldehyde is used as an intermediate in the manufacture of other organic compounds. The largest single outlet accounting for more than half of the acetaldehyde use is the manufacture of acetic acid. Other processes which utilize it as a raw material are the production of butyl alcohol, butyraldehyde, chloral and pyridine. (1)

There are four ways acetaldehyde can be made industrially. They are oxidation or dehydrogenation of ethanol, oxidation of ethylene in one or two stages, propane-butane oxidation and acetylene hydration. The oxidation or dehydrogenation of ethanol and ethylene oxidation are the major processes currently used. Ethylene oxidation is a relatively new method which is more attractive financially than ethanol oxidation because it utilizes a cheaper raw material. Although acetaldehyde via ethanol plants constitute about 44% of the current capacity no new plants of this type have been built in the last five years or are expected to be built in the future.

The decision as to which of the ethylene processes to use breaks down to a choice between lower initial investment costs for the one-stage process and lower raw material (air opposed to oxygen) costs for the two-stage process. The availability of cheap high grade oxygen is the prime determining factor. Currently the two-stage process is more popular in the U. S. but world wide both processes are being used extensively.

Air emission data presented in this report are from one respondent who uses the two-stage process. Because of the similarities of yields, catalyst type and separation techniques between the two processes, it is believed that air emissions for the one-stage method should be of the same order of magnitude as the two-stage method.

Air pollution released by a plant using the two-stage ethylene oxidation process can best be described as low. The main sources of air emissions are gases vented from the two scrubbers employed in the process.

(1) According to the Chemical Marketing Reporter for August 20, 1973, the current uses for acetaldehyde are:

Acetic Acid and Anhydride	50%
n-Butanol	14%
2-Ethyl Hexanol	11%
Other	25%

II. Process Description

The oxidation of ethylene to acetaldehyde is based on the reaction of aqueous palladium chloride with ethylene.

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2\ HCl$$

There are two versions of the process. In the 'two stage' version, ethylene is fed into a reactor with an aqueous solution of palladium chloride and cupric chloride. Ethylene is oxidized to acetaldehyde, and cupric chloride is reduced to cuprous chloride as a result of its oxidation of palladium back to palladium chloride. The actual reaction scheme is quite complex but the basic reaction reduces to:

$$C_2H_4 + 2\ CuCl_2 + H_2O \xrightarrow{PdCl_2} CH_3CHO + 2\ CuCl + 2\ HCl$$

In another reactor, which constitutes the second stage, cuprous chloride is oxidized back to cupric chloride with air completing the cycle

$$2\ CuCl + 2\ HCl + \tfrac{1}{2}\ O_2 \longrightarrow 2\ CuCl_2 + H_2O$$

In the 'one stage' version oxygen is fed into a reactor with ethylene. Both chlorides become catalytic for the reaction and the total process takes place in one reaction vessel.

$$C_2H_4 + \tfrac{1}{2}\ O_2 \xrightarrow[CuCl_2]{PdCl_2} CH_3CHO$$

The one stage process requires high purity ethylene and oxygen which could be a disadvantage depending on the availability of oxygen.

The following is a description of the two-stage ethylene oxidation technique. The separation methods for the single stage process are quite similar to the process described below. The only major difference between the two overall processes is the method of catalyst regeneration used and the need for ethylene recycle in the one stage process.

(See Figure ACD-I)
Ethylene is reacted at 10 atm. with a palladium chloride-cuprous chloride solution in a titanium lined tubular reactor. Conversion is about 99%. The acetaldehyde yield is around 95%; 1% of the ethylene does not react and the remainder forms by-products. The by-products include chloroacetaldehydes, ethyl chloride, chloroethanol, acetic and oxalic acids, crotonaldehyde and chlorocrotonaldehyde.

The reactor effluent is sent to a flash tower where the pressure is reduced to atmospheric and the heat of reaction is used to vaporize acetaldehyde and some water. The flash tower bottoms containing reduced catalyst solution is sent to an oxidizing reactor where the catalyst is regenerated by air oxidation. Unreacted oxygen, nitrogen and various other organics are purged off to a scrubber where some product and by-product are recovered and sent to distillation, while gases leaving the scrubber are vented to the atmosphere. Regenerated catalyst is returned to the reactor.

Flashed gas passes to a crude acetaldehyde still where acetaldehyde is distilled to 60 - 90%. Light ends are removed next, in another column. Gas exiting from the top of this tower is water scrubbed and then vented to the atmosphere. The acetaldehyde leaves the bottom of the light ends column and enters a finishing column where chloroaldehydes, water and other undesirables are removed. Finished acetaldehyde is taken overhead and sent to storage.

A material balance and information on the heat liberated by reaction can be found in Tables I and II, respectively.

III. Plant Emissions

A. Continuous Air Emissions

1. Regenerator Off-Gas Scrubber Vent

After the catalyst is regenerated with air the gaseous stream is purged from the reactor system and scrubbed to recover water soluble organics, while the solution of regenerated catalyst is returned to the reactor. The stream leaving the scrubber is vented to the atmosphere. Since nitrogen in the air does not react, it is the primary component present in the vent gas. Quantities of argon, unreacted oxygen, water, carbon dioxide and smaller amounts of methyl and ethyl chloride also enter the atmosphere through this vent. Total hydrocarbon emissions are reported to be .00045 lbs./lb. acetaldehyde from this source.

NOTE: Calculations made by Houdry show that it is possible that the average flow rate of this stream could be twice as high as that claimed by the respondent.

2. Light Ends Scrubber Vent

Light ends consisting of nitrogen, carbon dioxide, ethylene, methyl and ethyl chloride and water soluble oxygenated hydrocarbons including acetaldehyde and acetic acid are removed from the system by crude distillation and light ends distillation and are sent to a water scrubber. Water soluble vapors are removed in the scrubber and the insoluble gas is vented to the atmosphere. The air pollutants released through this vent are methyl chloride, ethyl chloride and ethylene. Hydrocarbon emissions are usually around .00047 lbs./lb. acetaldehyde from this source but emissions could vary because the flow rate can change by 500%.

B. Intermittent Air Emissions

No sources of intermittent air emissions were reported by the respondent.

C. Continuous Liquid Wastes

Approximately 150 GPM of waste water is discharged. The effluent is treated in biological aerated ponds with solar evaporation.

D. Solid Waste

About one ton of solid waste, consisting mainly of spent catalyst, is disposed of in a sanitary land fill, per day.

E. Odor

In general the ethylene process for the production of acetaldehyde does not appear to present an odor problem. No community complaints have been reported.

F. Fugitive Emissions and Storage Losses

The respondent reports that losses due to leaks and spills are too small to measure.

Acetaldehyde storage tanks are vented to a scrubber so no acetaldehyde enters the atmosphere from the storage area.

IV. Emission Control

Usually efficiencies are calculated for any emission control device reported, but since the only respondent to the questionnaire failed to supply information about the composition and flow of the inlet streams to the devices employed, it was impossible to do so. A brief description of these devices follows: Details concerning the emission control equipment employed can be found in Table IV - Catalog of Emission Control Devices.

Scrubbers

A. Off Air Scrubber

This scrubber removes any soluble organics such as acetaldehyde, acetic acid and chloroaldehydes which may be present in the nitrogen and unreacted oxygen stream which is purged from the reaction area. Since no acetaldehyde, acetic acid or chloroacetaldehyde are present in the vent gas, the efficiency of removal for these components is 100%. The liquid outlet from this scrubber is sent to the purification system.

B. Light Ends Scrubber

Light components from the crude still, light ends column and product storage tanks are sent to this scrubber for soluble organics recovery. The liquid effluent is returned to the purification system. Almost all soluble components are removed by this scrubber.

C. Water Insolubles

Both of the above vent streams contain traces of methyl and ethyl chlorides and the light ends scrubber vent also contains unreacted ethylene. All three of these chemicals are only slightly soluble in water so the efficiency relative to each is near zero percent.

V. Significance of Pollution

It is recommended that no in-depth study of the ethylene process for acetaldehyde be made at this time. The reported emission data indicate that the quantity of pollutants released to the atmosphere as air emissions is less for the subject process than for processes currently under in-depth study.

The methods outlined in Appendix IV of this report have been used to estimate the total weighted annual emissions from new plants. This work is summarized in Tables V, VI and VII. The growth projection is based on the assumption that all new acetaldehyde plants will use the ethylene process.

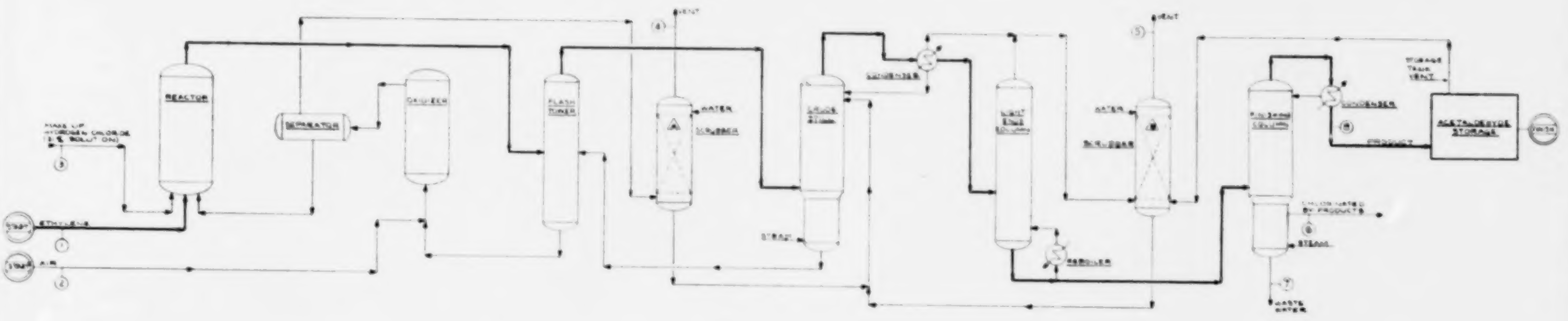
On a weighted emission basis a Significant Emission Index of 96 has been calculated in Table VII. Hence, the recommendation to exclude the subject process from the in-depth portion of the work for this project.

However, it should be noted that reported emissions, especially of ethylene, do not agree with literature reports on the ethylene conversion of 99%. Since the process is "once-through" with respect to ethylene, one volume percent of unconverted ethylene would be equivalent to nearly 0.007 lbs. of ethylene vented/lb. of acetaldehyde product (at 95% yield). On this basis, the calculated SEI would increase to about 780.

VI. Acetaldehyde Producers

The following tabulation of acetaldehyde producers indicates production capacity by company, location and process.

		Butane Propane	By-Product	Ethanol	Ethylene 1 Stage	Ethylene 2 Stage
Celanese	Bay City, Texas					210
	Bishop, Texas					
	Pampa, Texas		10			
	Clear Lake, Texas					500
Commercial Solvents	Agnew, California			1		
Du Pont	Belle, W. Va.		10			
Eastman	Kingsport, Tenn.			200		
	Longview, Texas					450
Goodrich	Calvert, City		1			
Hercules	Parlin, N. J.			35		
Monsanto	Texas City, Texas		5			
Publicker	Philadelphia, Pa.			80		
Union Carbide	Institute, W. Va.)					
	South Charleston, W. Va.)			650		
	Texas City, Texas)					
		Total MM Lbs./Yr.	= 26	966		1,160


MAKE UP HYDROGEN CHLORIDE (3% SOLUTION)
3
START ETHYLENE
1
START AIR
2
REACTOR
SEPARATOR
OXIDIZER
FLASH TOWER
4
VENT
WATER
SCRUBBER
A
STEAM
CRUDE STILL
CONDENSER
LIGHT ENDS COLUMN
REBOILER
5
VENT
WATER
SCRUBBER
A
REFINING COLUMN
CONDENSER
8
PRODUCT
STORAGE TANK VENT
ACETALDEHYDE STORAGE
FINISH
CHLORINATED BY PRODUCTS
6
STEAM
7
WASTE WATER

NOTES

1. NUMBERED STREAMS ARE CROSS-REFERENCE IDENTITIES FOR MATERIAL BALANCE TABLE I AND NATIONAL EMISSIONS INVENTORY - TABLE II
2. LETTERED DEVICES ARE DESCRIBED IN CATALOG OF EMISSION CONTROL DEVICES TABLE III.

ENVIRONMENTAL PROTECTION AGENCY
CONTRACT No 68-02-0255

PREPARED BY
[illegible]

FIGURE AC5
SIMPLIFIED FLOW DIAGRAM
ACETALDEHYDE VIA
TWO-STAGE ETHYLENE PROCESS

[illegible]	NONE	[illegible]
[illegible]	TTMA	[illegible]
[illegible]	GMF	[illegible]
[illegible]		
[illegible]	[illegible]	[illegible]

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TABLE ACD-I
MATERIAL BALANCE
T/T ACETALDEHYDE
VIA
ETHYLENE PROCESS

Stream I. D. No.	1	2	3	4	5	6	7	8
Stream	Ethylene Feed	Air	Make-Up HCl (31%)	Off-Air Scrubber Vent (3)	Light Ends Scrubber Vent (3)	By-Products	Water to Waste (1)	Product
Component								
Ethylene	.6570				.0013			
Air								
1) Nitrogen		1.3739		1.3739				
2) Oxygen		.4209		.0086				
3) Argon		.0233		.0233				
Make-Up HCl			.0100					
Acetaldehyde			.0323 (2)					1.0000
Carbon Dioxide				.0166	.0230			
Water				.0001	.0001		.0482	
Methyl Chloride				.0008	.0004			
Ethyl Chloride				.0001	.0008			
Chloroaldehydes						.0187		
Acetic Acid						.0015		
	.6570	1.8181	.0423	1.4234	.0256	.0202	.0482	1.0000

Total In = 2.5174

Total Out = 2.5174

(1) Water formed by side combustion reactions and water from make-up HCl solution only; recycled water and other process water introduced into the system not included; contains some hydrocarbon.

(2) Contained in recycled water used as HCl diluent.

(3) Vent streams show emissions somewhat greater than reported in the single questionnaire.

TABLE ACD-II
HEAT BALANCE
ACETALDEHYDE
VIA
ETHYLENE PROCESS

There is insufficient information available on which to base an overall heat balance for this process.

Overall Heat of Reaction for Reaction and Regeneration Steps

$$C_2H_4\ (g) + \tfrac{1}{2}\ O_2\ (g) \longrightarrow CH_3CHO\ (g)$$

H = 2,210 BTU/lb. acetaldehyde

TABLE ACD-III
NATIONAL EMISSIONS INVENTORY
ACETALDEHYDE
VIA
ETHYLENE PROCESS

EPA Plant Code No.	1-2	
Capacity - Tons of Acetaldehyde/Yr.	225,000	
Production - Tons of Acetaldehyde/Yr.	220,000	
Emissions to the Atmosphere		
Stream I. D. No.	4	5
Stream	Regenerator Off-Gas Scrubber Vent	Light Ends Scrubber Vent
Flow - Lbs./Hr.	40,871 (1)	2675 (1)
Flow Characteristic - Continuous or Intermit**tent**	Continuous	Continuous
If Intermittent - Hrs./Yr.		
Composition - Tons/Ton of Acetaldehyde		
Ethylene		.00025
Methyl Chloride	.00041	.00007
Ethyl Chloride	.00004	.00015
Carbon Dioxide	.00828	.00459
Water	.00040	
Nitrogen	.74524	.00502 (2)
Argon	.01288	
Oxygen	.00430	
Analysis	Yes	Yes
Sample Tap Location	In **stream**	In **stream**
Frequency of Sampling	C_2H_4 & CO_2 Continuous - Others **Weekly**	C_2H_4 & CO_2 Continuous - Others **Weekly**
Type of Analysis	C_2H_4 **Infrared** - Others **Chromatograph**	C_2H_4 & CO_2 **Infrared - Others Chromatograph**
Odor Problem	No	No
Vent Stacks	Yes	Yes
Number	2 (3)	2 (3)
Height - Ft.	100	80
Diameter - Inches	16	4
Exit Gas Temperature - F°	59	59
SCFM	4500	50
Emission Control Devices	Yes	Yes
Type	Scrubber	**Scrubber**
Summary of Air Pollutants		
Hydrocarbons - Ton/Ton of Acetaldehyde	.00092	
Particulates - Ton/Ton of Acetaldehyde	0	
NO_x - Ton/Ton of Acetaldehyde	0	
SO_x - Ton/Ton of Acetaldehyde	0	
CO - Ton/Ton of Acetaldehyde	0	

(1) **Plant has two identical** systems so actually two identical scrubbers of this type **are employed**. Flow is **total for each scurbber.**

(2) From **acetaldehyde** storage tank purge.

(3) For **each** scrubber.

TABLE ACD-IV
CATALOG OF EMISSION CONTROL DEVICES
ACETALDEHYDE
VIA
ETHYLENE PROCESS

ABSORBERS/SCRUBBERS	(1)		(1)	
EPA Code No. for plant using	1-2		1-2	
Flow Diagram (Fig. ACT-I) Stream I. D.	A		B	
Control Emission of	Organic Vapors (2)		Organic Vapors (2)	
Scrubbing/Absorbing Liquid	Water		Water	
Type - Spray				
Packed Column	Yes		Yes	
Column w/Trays				
Scrubbing/Absorbing Liquid Rate - GPM				
Operating Temperature - F°	62.5 - 140		62.5 - 140	
Gas Rate - SCFM	4500 - 8000		50 - 250	
T-T Height - Ft.	90		70	
Diameter - Ft.	5		3	
Washed Gases to Stack	Yes		Yes	
Stack Height - Ft.	100 (3)		80 (3)	
Stack Diameter - Inches	16		4	
Installed Cost - Mat'l. & Labor - $	410,000	490,000	255,000	275,000
Installed Cost based on "year" - $	1965	1969	1965	1969
Installed Cost - ¢/lb. of Acetaldehyde/Yr.	.20		.12	
Operating Cost - Annual - $ - 1972	45,000		26,500	
Value of Recovered Product - $/Yr.	Unknown		Unknown	
Net Operating Cost - ¢/lb. of Acetaldehyde	.01		.006	
Efficiency - % - SE				
Efficiency - % - SERR				

(1) Two identical scrubbers of each type are employed. Specifications are for each scrubber, a total of four scrubbers are used for emission control in the process. Cost figures are the combined costs for two identical scrubbers.

(2) Acetaldehyde, acetic acid and some chlorohydrocarbons

(3) Each scrubber has two stacks, each stack has specifications shown.

TABLE ACD-V
NUMBER OF NEW PLANTS BY 1980
ACETALDEHYDE
VIA
ETHYLENE OXIDATION

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Plants
1160	0	1160	2460 (1)	2460	1300 (2)	250	5 - 6

(1) For ethylene process.

(2) Based on studies prepared for the EPA by Process Research, Inc.

TABLE ACD-VI
EMISSION SOURCE SUMMARY
ACETALDEHYDE
VIA
ETHYLENE PROCESS

Emission	Source		Total
	Regenerator Off-Gas Scrubber Vent	Light Ends Scrubber Vent	
Hydrocarbons	.00045	.00047	.00092
Particulates	0	0	0
NO_x	0	0	0
SO_x	0	0	0
CO	0	0	0

TABLE ACD-VII
WEIGHTED EMISSION RATES

Chemical Acetaldehyde

Process Ethylene

Increased Capacity 1300 MM Lbs./Year

Pollutant	Emissions lb./lb.	Emissions MM lbs./yr.	Weighting Factor	Weighted Emissions MM lbs./yr.
Hydrocarbons	.00092	1.2	80	96
Particulates	0	0	60	0
NO_x	0	0	40	0
SO_x	0	0	20	0
CO	0	0	1	0

Significant Emission Index = 96

Acetaldehyde via Ethanol

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I. Introduction

Acetaldehyde (CH_3CHO) is a mobile, colorless, inflammable liquid with a pungent, choking odor. It was first noticed by Scheele in 1774 and recognized as a new compound by Foucroy and Vaughelin in 1880.

Most acetaldehyde is used as an intermediate in the manufacture of other organic compounds. The largest single outlet accounting for more than half of the acetaldehyde use, is the manufacture of acetic acid. Other processes which utilize it as a raw material are the production of butyl alcohol, butyraldehyde, chloral and pyridine.

There are four ways that acetaldehyde can be made industrially. They are the oxidation or dehydrogenation of ethanol, oxidation of ethylene in one or two stages, propane-butane oxidation and acetylene hydration. The oxidation or dehydrogenation of ethanol and ethylene oxidation are the major processes currently used. Ethylene oxidation is a relatively new method which is more attractive financially than ethanol oxidation because it utilizes a cheaper raw material. Although acetaldehyde via ethanol plants constitute 43.8% of the current capacity of 2.4 billion lbs./year no new plants of this type have been built in the last five years or are expected to be built in the future.

Atmospheric emissions generated by the ethanol process are associated primarily with the absorber vent gas stream. All other sources of emissions are minimal.

It should be noted that this report is based on the responses of one questionnaire. The only respondent was a plant using ethanol oxidation and, therefore, the straight dehydrogenation of ethanol is covered only briefly in Section V.

II. Process Description

Acetaldehyde is produced by passing ethanol vapors and preheated air over a suitable catalyst, preferably silver, at 300 - 575° C.

Two possible reactions occur to varying degrees depending on the reactor environment.

(1) $C_2H_5OH + \frac{1}{2} O_2 \longrightarrow CH_3CHO + H_2O$ $\quad H = -40.55$ kcal./g-mole

(2) $C_2H_5OH \longrightarrow CH_3CHO + H_2$ $\quad H = +17.28$ kcal./g-mole

Industrially oxidation, a combination of oxidation and dehydrogenation and straight dehydrogenation (which is not covered in this report) are used. The reactor temperature depends on the air-ethanol-steam ratio and the velocity of the gas over the catalyst. Overall alcohol conversion varies from 25 - 45% and yields are 85 to 95%. Small amounts of acetic acid and 1-butanol are also formed. Many times dilute acetic acid is recovered as a by-product.

The gases leaving the reactor, after passing through a condenser, go to a phase separator. The vapor phase is absorbed in refrigerated water, and the wash is combined with the liquid phase. The combined stream is fractionated into acetaldehyde and a water-ethanol mixture, which is further separated into ethanol, which is recycled, and waste acetic acid can be recovered from the waste.

III. Plant Emissions

A. Continuous Air Emissions

1. Absorber Vent

The emissions from this vent constitute the most important source of air pollution associated with the production of acetaldehyde by oxidation. In comparison, all other sources of air pollution are minimal.

The vent stream is composed primarily of nitrogen. Small quantities of water, carbon dioxide, carbon monoxide, hydrogen methane and oxygen are also present. Plant 1-1 reports the following emissions from the scrubber vent stream.

Component	Lbs./Lb. Acetaldehyde
Water	.00088
CO	.00271
CO_2	.00934
H_2	1.12450
CH_4	.01950
O_2	.02240

A more complete description of emissions can be found in Table III.

B. Intermittent Air Emissions

1. Combustion of Fuel for Reactor Start-Up

The respondent reports that 480,000 CF/year of natural gas with sulfur content of 2.0 grains/100 CF are needed to start the reactors. If the sulfur content of this fuel is fully converted into sulfur dioxide, it would produce 2.8 lbs of SO_2 per year, which is 1.6×10^{-8} lbs. SO_2/lb. product. This quantity is considered negligible.

2. Ethanol Storage Tank Vent

Inert gases are periodically purged from the ethanol storage tank. During venting small amounts of ethanol are released to the atmosphere. Lack of data prevents the calculation of emission rates, but this vent could not be considered a significant emission source.

C. Continuous Liquid Wastes

16,000 gallons per hour of waste water is produced. The respondent reports that waste water is treated on-site.

D. Solid Wastes

No solid wastes are produced by this process.

E. Odor

No odor problems were reported for the ethanol oxidation process for the production of acetaldehyde.

F. Fugitive Emissions

No sources of fugitive emissions were reported. If they exist, they are probably due to minor losses of acetaldehyde and/or ethanol due to pump seals and occasional piping leaks. The actual amount is considered negligible.

IV. Emission Control

The only emission control device reported is a scrubber system. It is summarily described in Table IV of this report. Two types of efficiencies have been calculated.

1) SE - Specific Efficiency

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

2) SERR - Significance of Emission Reduction Rating

$$SERR = \frac{(\text{pollutant} \times \text{weighting factor})\text{in} - (\text{pollutant} \times \text{weighting factor}^{*})\text{out}}{(\text{pollutant} \times \text{weighting factor})\text{in}} \times 100$$

A more complete description of the rating system can be found in Appendix V of this report.

*weighting factor same as Table VII weighting factor.

Absorbers

Although the respondent lists the two scrubbers as emission control devices their primary function is the recovery of acetaldehyde and ethanol. Alcohol and acetaldehyde recovery is 100 percent while practically no CO is removed. However, the SERR is greater than 99.9 percent because of the relatively small quantity of CO present as well as its low weighting factor.

V. Significance of Pollution

It is recommended that no in-depth study of this process be undertaken at this time. This conclusion is drawn for two reasons.

1) The reported emission data indicate the quantity of pollutants released as air emissions is less for the subject process than for other processes that are currently being surveyed.

2) No new plants are expected to be built using ethanol as the starting material. New production will probably rely on the ethylene oxidation processes which are already taking a large role in acetaldehyde production. Some of the advantages of using the ethylene oxidation processes are listed below:

   a) Uses a less expensive starting material - ethylene.

   b) Utilizes a shorter route from hydrocarbon to acetaldehyde.

   c) Products yields of approximately 95 percent.

   d) Operates at low temperatures and pressures.

The outlook is for acetaldehyde capacity to grow to three to five billion pounds per year by 1980, which will require four or five new plants which are expected to be of the ethylene oxidation type.

The methods outlined in Appendix IV of this report have been used to estimate the total weighted annual emissions from new plants. This work is summarized in Tables V, VI and VII.

On a weighted emission basis a Significant Emission Index of zero has been calculated in Table VII, due to the fact that no new ethanol oxidation plants are expected to be built. Since the total emissions from this process are small and no growth is anticipated, it is recommended to exclude acetaldehyde production via ethanol oxidation for an in-depth study.

In passing, something should be said about the straight ethanol dehydrogenation process which is not covered in this report. Due to the fact that no oxygen is introduced in the system it appears that the total amount of emissions released to the atmosphere should be minimal. This prediction is confirmed by limited data made available by the EPA, Raleigh, N. C. Emissions from a typical ethanol dehydrogenation plant are: A once/week vent for one minute at a rate of 50,000 CFH of a stream whose typical composition is:

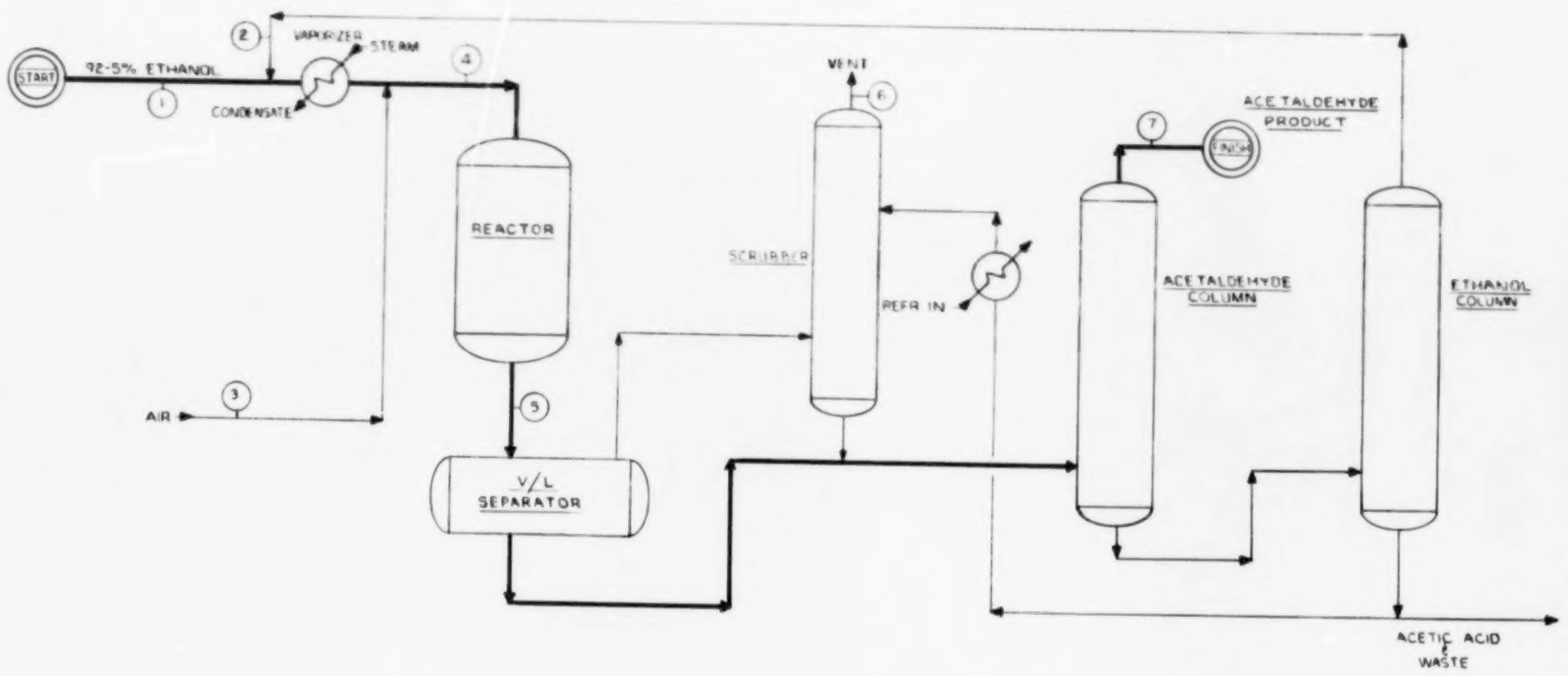
Component	Volume %
Hydrogen	98.5
Methane	.8
Carbon Monoxide	.3
Ethane	.1
Carbon Dioxide	.3

The plant mentioned produced 27,190 lbs./hr. of acetaldehyde. The quantity of emission is quite small in comparison to other processes studied.

VI. Acetaldehyde Producers

The following tabulation of acetaldehyde producers indicates published production capacity by company, location and process.

Company	Location	Butane - Propane	By-Product	Ethanol	Ethylene 1 Stage	Ethylene 2 Stage
Celanese	Bay City, Texas					210 (1962)
	Bishop, Texas					
	Pampa, Texas		10			
	Clear Lake, Texas					500
Commercial Solvents	Agnew, California			1		
Du Pont	Belle, W. Va.		10			
Eastman	Kingsport, Tenn.			200		
	Longview, Texas					500 (1970)
Hercules	Parlin, N. J.			35		
Monsanto	Texas City, Texas		5			
Publicker	Philadelphia, Pa.			80		
Union Carbide	Institute, W. Va.) South Charleston, W. Va.) Texas City, Texas)			650		
		Total MM Lbs./Yr. =	25	966		1,210
		% Grand Total =	1.3	43.8		54.9


START
92-5% ETHANOL
1
2
VAPORIZER
STEAM
CONDENSATE
4
AIR
3
REACTOR
5
V/L
SEPARATOR
VENT
6
SCRUBBER
REFR IN
7
FINISH
ACETALDEHYDE
PRODUCT
ACETALDEHYDE
COLUMN
ETHANOL
COLUMN
ACETIC ACID
&
WASTE

NOTES

1) NUMBERED STREAMS ARE CROSS-REFERENCE IDENTITIES FOR MATERIAL BALANCE AND CATALOG OF EMISSION CONTROL DEVICES - TABLE IV

FOR
ENVIORMENTAL PROTECTION AGENCY
CONTRACT NO. 68-02-0255

PREPARED BY
CATALYTIC, INC.
ENGINEERING DEPARTMENT, PHILADELPHIA, PENNA. 19102

FIGURE AC-1
SIMPLIFIED FLOW DIAGRAM OF
ACETALDEHYDE VIA
ETHANOL OXIDATION

		DATE
SCALE	NONE	
DRAWN BY	T.M. PEASE	4-14-73
CHECKED BY	E.T.	4-17-73
CATALYTIC APPROVAL		
CLIENT APPROVAL		4-19-73

PROJECT NO. 42030
I.D. NO. 423
DWG. NO. R-228
REV. NO. A

TABLE AC-1
ACETALDEHYDE
VIA
ETHANOL OXIDATION

MATERIAL BALANCE - T/T OF ACETALDEHYDE

Stream I. D. No.	1		2	3	4	5	6	7	8	
	Fresh Feed	Water	Recycle Ethanol	Air	Gross Feed	Reactor Effluent	Off-Gas	Product	By-Product 5% Acid	Waste
Ethanol	1.1066	.0592	.0592		1.1658	.0592				
Acetaldehyde						1.0000		1.0000		
Water/Steam		.0897			.0897	.4920	.0009		.0638	.4273
Oxygen				.3575	.3575	.0224	.0224			
Carbon Monoxide						.0027	.0027			
Methane						.0020	.0020			
Carbon Dioxide						.0093	.0093			
Hydrogen						.0149	.0149			
Nitrogen				1.1769	1.1769	1.1769	1.1769			
Acetic Acid						.0032			.0032	
Oxygenatic Organics						.0073				.0073
Total	1.1066	.0897	.0592	1.5334	2.7899	2.7899	1.2291	1.0000	.0670	.4346

TABLE AC-II
ACETALDEHYDE
VIA
ETHANOL OXIDATION

There are not sufficient data to permit the construction of an overall heat balance for this process.

Heat Generated by Reaction

$C_2H_5OH + \frac{1}{2} O_2 \longrightarrow CH_3CHO + H_2O$ H = -44.55 kcal./mole

$C_2H_5OH \longrightarrow CH_3CHO + H_2O$ H = +17.28 kcal./mole

97.8% Oxidation
2.2% Dehydration

Heat evolved by reaction = 1,763 BTU/lb. acetaldehyde

TABLE AC-III
NATIONAL EMISSIONS INVENTORY
ACETALDEHYDE
VIA
ETHANOL OXIDATION

EPA Plant Code No.	1-1
Capacity, Tons of Acetaldehyde/Yr.	90,000
Range in Production - % of Max.	Not Specified
Emissions to Atmosphere	
Stream	Absorber Vent
Flow - Lbs./Hr.	24,426
Flow Characteristic - Continuous or Intermittent	Continuous
if Intermittent - Hrs./Yr.	
Composition - Tons/Ton of Acetaldehyde	
Methane	.00195
Carbon Monoxide	.00276
Carbon Dioxide	.00934
Hydrogen	.01491
Nitrogen	1.12450
Oxygen	.02239
Water	.00934
Sample Tap Locations	Not Specified
Frequency of Sampling	Three times per week
Type of Analysis	Gas Chromatography
Odor Problem	No
Vent Stacks	
Flow - SCFM/Stack	6,500
Number	3
Height - Feet (elev. @ tip)	75
Diameter - Inches	792
Exit Gas Temperature - F°	45
Emission Control Devices	
Type	Two water scrubbers
Summary of Air Pollutants	
Hydrocarbons - Ton/Ton Acetaldehyde	0
Particulates - Ton/Ton Acetaldehyde	0
NO_x - Ton/Ton Acetaldehyde	0
SO_x - Ton/Ton Acetaldehyde	0
CO - Ton/Ton Acetaldehyde	.00276

TABLE AC-IV
CATALOG OF EMISSION CONTROL DEVICES
ACETALDEHYDE
VIA
ETHANOL OXIDATION

ABSORBER/SCRUBBER		
EPA Code No. for plant using	1-1	
Flow Diagram (Fig. I) Stream I. D.	6	
Control Emission of	Water Soluble Organics	
Scrubbing/Absorbing Liquid	Water	
Type - Spray		
Packed Column		
Column w/trays*	X	
Number of trays	29	25
Tray type	Bubble Cap	Bubble Cap
Other		
Scrubbing/Absorbing Liquid Rate - GPM	170	170
Design Temp. (Operating Temp.) F°	45°	45°
Gas Rate - SCFM	6,500	6,500
T-T Height, Ft.	Not Specified	
Diameter - Inches	96	60
Washed Gases to Stack**	No	Yes
Stack Height - Feet		75 ft.
Stack Diameter - Inches		3 at 66 each
Installed Cost - Mat'l. & Labor - $	80,000	95,000
Installed Cost based on - "year" - $	1938	1940
Installed Cost ¢/lb. of acetaldehyde/Yr.	.102	
Operating Cost - Annual - $ - 1972	55,330	
Value of Recovered Product - $/Yr.	2,275,000	
Net Operating Cost - ¢/lb. of Acetaldehyde	(2,219,670)	
Efficiency - % - SE	100	
Efficiency - % - SERR	99.9+	

TABLE AC-V
NUMBER OF NEW PLANTS BY 1980

ACETALDEHYDE VIA ALL PROCESSES

Current Capacity (1)	Marginal Capacity	Current Capacity on-stream in 1980	Demand in 1980	Capacity to be Added	Economic Plant Size	Number of New Plants
2,402	(2)	2,202 (3)	3,500 (4)	1,298	200	5

ACETALDEHYDE ETHANOL OXIDATION AND/OR DEHYDROGENATION

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand in 1980	Capacity to be Added	Economic Plant Size	Number of New Plants
966 (5)	(2)	966	966 (6)	0	100	0

(1) All capacities in MM lbs./year.

(2) No data is available.

(3) Assumed 0 marginal capacity - it is possible that all plants using the ethanol process will be operating since many manufacture acetic acid directly from the acetaldehyde produced.

(4) C & E News, May 17, 1971.
The Petrochemical Industry Markets & Economics, 1970.

(5) Include acetaldehyde produced by straight dehydrogenation.

(6) Assumes no new ethanol plants will be built and no capacity will be lost.

TABLE AC-VI
EMISSION SOURCE SUMMARY
T/T OF ACETALDEHYDE

Emission	Source		
	Absorbent Vent	Fuel for Reactor Start-Up	Ethanol Storage Vent
Hydrocarbons	0	Negligible	Negligible
Particulates	0		
NO_x	0		
SO_x	0		
CO	.00276		

TABLE AC-VII
WEIGHTED EMISSION RATES

Chemical Acetaldehyde

Process Ethanol Oxidation

Increased Capacity* 0.0 Lbs./Yr.

Pollutant	Emissions Lbs./Lb.	Increased Emissions MM Lbs./Year	Weighting Factor	Weighted Emissions MM Lbs./Year
Hydrocarbons	None		80	
Particulates	None		60	
NO_x	None		40	
SO_x	Negligible		20	
CO	.00276	0.0	1	0.0

Significant Emissions Index = 0.0 MM Lbs./Yr.

NOTE

*No new ethanol oxidation or dehydration plants are expected to be built.

Acetic Acid via Methanol

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I. Introduction

Acetic acid passed the billion lb./year mark ten years ago and has continued to be one of the fastest growing of all chemicals. All of the growth in acetic acid production for the past 20 years has been via new synthetic routes. Destructive distillation of wood to give acetic acid, methanol and by-products is a dying process and has been on a steady decline since 1950. There are three main synthetic processes currently in use for acetic acid production in the United States.

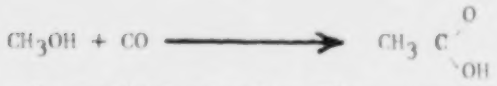
Process	Raw Materials	Approximate % of 1972 Production
1. Oxidation of hydrocarbons (LPG)	mainly butane	43
2. Oxidation of acetaldehyde	acetaldehyde	31
3. Carbonylation of methanol	CH_3OH and CO	16

The largest single use for acetic acid is in the production of acetic anhydride which, in turn, goes into the production of cellulose acetate for fibers. A second large use is the production of vinyl acetate used in vinyl plastics, paints, adhesives and textile finishes. Acetate esters, chloroacetic acid, nylon and acrylic fibers (chain terminator), and pharmaceuticals make up the rest of the major uses of acetic acid.

This report covers acetic acid made from the newest of the synthetic routes, carbonylation of methanol. Reactants for this process are methanol and a "synthesis gas" composed mainly of H_2, CO, CO_2 and hydrocarbons. Two variants of the process are in use; both are moderate temperature (480° F) liquid phase reaction but pressures range from comparatively low to near 10,000 PSI. A brief scanning of the reactants used shows that this process could be a large source of air pollution if excess synthesis gas were vented directly to the air. However, since reactants and products are hydrocarbons or oxygen containing organics only, proper flaring or incineration of vented gases will produce only CO_2 and water with no NO_x or SO_x. This appears to be the case for the data supplied by the respondents indicating little or no pollutants emitted from these plants. Of course, since atmospheric air is required in the flaring operation, some NO_x is probably produced by oxidation of the atmospheric nitrogen.

II. Process Description

The main reaction involved in the carbonylation of methanol is·



$$CH_3OH + CO \longrightarrow CH_3C\begin{matrix}\nearrow O \\ \searrow OH\end{matrix}$$

a by-product reaction also gives

$$CO + H_2O \longrightarrow CO_2 + H_2$$

Other by-products formed are methyl acetate, dimethyl ether, formic acid, propionic acid and water. All secondary reactions are reversible, fortunately, and can be minimized or eliminated by proper choice of operating conditions. The first successful process involving the carbonylation of methanol in the U. S. was the BASF process which uses temperatures around 500° F and pressures of 7500 to 10,000 PSI. It is a liquid phase reaction. Choice of catalyst is highly critical for good yields. Cobalt Iodide is one such catalyst. Monsanto uses a similar process but their catalyst, reportedly a "Rhodium and Iodine containing system" from the literature, enables them to carry out the reactions at a much lower pressure than the BASF process.

Reacted products are stripped of light ends, scrubbed and vented to the air via a flare or incinerator. There is a recycle stream back to the reactor. Crude acetic acid is then purified by distillation. Either conventional rectification with a "wet acid" recycle stream or azeotropic distillation is used. Most by-products are returned to the reaction system where they become recycled to extinction. A "heavy" stream of mixed acetic and propionic acids is removed from the distillation section and incinerated. Ultra pure (99.8+%) acetic acid is the main product.

Yields of 99+% of acetic acid on methanol and over 90% on CO are reported in the literature and data from the respondents confirm these figures. Only small amounts of by-products are produced.

III. Plant Emissions

A. Continuous Air Emissions

1. Purification Section Vents

Light ends and unreacted (or excess) synthesis gases are scrubbed and flared or incinerated by both respondents. No data are available on the composition of the combusted gases. However, analyses are available for the gas streams as they go to incineration. If the incinerator (flare) is operating properly and is well designed for complete combustion, there is no reason to believe that these gases will not be converted completely to CO_2 and water. No nitrogen or sulfur compounds are present. Possibly some CO could be emitted but this should be minimal with a good incinerator or flare. As a result, we have assumed pollutant emissions from this source as nil, except for 20 to 40 ppm of NO_x generated by the oxidation of atmospheric nitrogen.

B. Intermittent Air Emissions

1. Catalyst System Purge Gas

One respondent reports an intermittent purging of his catalyst make-up system with air. Some iodine vapor (0 - 1000 PPM) escapes with the air. This is reported as completely removed by a sodium carbonate absorber and, hence, emissions from this source are nil.

C. Continuous Liquid Wastes

A stream of mixed acetic and propionic acid is removed from the purification section and sent to incineration. No data are available on the incinerated gases from this stream. Apparently, both respondents sent this stream to a plant incinerator along with other waste streams. There is nothing about this stream that would preclude it being burned completely to CO_2 and water only. Once again, emission of pollutants would be nil.

D. Solid Wastes

There were no solid waste reported for this process.

E. Odors

When operating properly, there does not seem to be an odor problem associated with this process. All vent gases are incinerated to CO_2 and water. Only one respondent indicated a possible odor problem. In this plant (presumably the other plant has a similar vent) there is an emergency vent in the purification system which vents pure acetic acid vapor to the atmosphere for 10 - 15 minutes in the event of a total power failure. In this emergency condition the odor of acetic acid was obviously evident in and around the plant but no complaints were reported. This appears to be only isolated instances so in general, the plant seems to be relatively clean and free of atmospheric pollutants. Some emergency vents are flared.

F. Fugitive Emissions

No fugitive emissions are mentioned. Since both plants handle gas streams containing CO one would imagine that any leaks whatsoever would receive prompt attention, if only for operator safety.

G. Other Emissions

One respondent has a vapor conservation system consisting of a nitrogen blanket and conservation vents on all product and raw material storage tanks. They vent to the atmosphere during filling or from solar heating. No estimate of emissions was made, but some must occur.

IV. Emission Control

Emission control devices employed in this process are summarized in Table IV. Unfortunately, there are very little data available on these devices, as is true with most incineration systems. As mentioned previously, composition of the streams going to incineration or flaring are such that complete combustion would lead to only CO_2 and water. Calculation of any efficiencies or emission indices for these devices in the absence of flue gas composition becomes meaningless for one can only assume 100% combustion and, therefore, 100% efficiency, except for some formation of NO_x.

One respondent uses a sodium carbonate absorber to remove iodine vapor from purge air from his catalyst preparation system. This is an intermittent stream and is reported as 100% absorbed in the sodium carbonate. Its efficiency is, therefore, 100%.

V. Significance of Pollution

We recommend that no in-depth study of this process be made. Present technology is more than adequate to give a virtually air pollutant free plant if the devices are used properly. All waste streams are capable of incineration to CO_2 and water. Assuming that any new plant using this process would employ similar pollution control devices, there should be no atmospheric emissions from this process other than emergency venting due to power failures and the like.

VI. Producers of Acetic Acid - All Routes Shown

Company	Location	MM Lbs./Yr.	Route
Borden, Inc.	Geismar, La.	100	Carbonylation of Methanol
Celanese	Bayport, Texas	300	Acetaldehyde
	Bishop, Texas	150	"
	Pampa, Texas	500	Oxidation of butane
Eastman Chemical Prod.	Kingsport, Tenn	325	Acetaldehyde
FMC, Organic Chem. Div.	Bayport, Texas	45	Glycerine by-product
Forest Prod.	Memphis, Tenn.	N. A	Wood Distillation
Hercules, Inc.	Parlin, N. J.	40*	By-product
Kingsford Chem. Co.	Iron Mtn., Mich.	N. A.	Wood Distillation
Monsanto	Texas City, Texas	300	Carbonylation of Methanol
Publicker Industries	Philadelphia, Pa.	80	Fermentation by-product
Sonoco Prod. Co.	Hartsville, S. C.	N. A	Extraction
Union Carbide	Brownsville, Texas	500	Oxidation of butane
	Taft, La.	90	Caprolactone by-product
	Texas City, Texas	100*	Acetaldehyde
Mobil Chemical	Beaumont, Texas	30	Terephthallic acid By-product
		2,420** on stream	

*140 on stand-by

**400 from carbonylation of methanol or 17% of installed capacity.

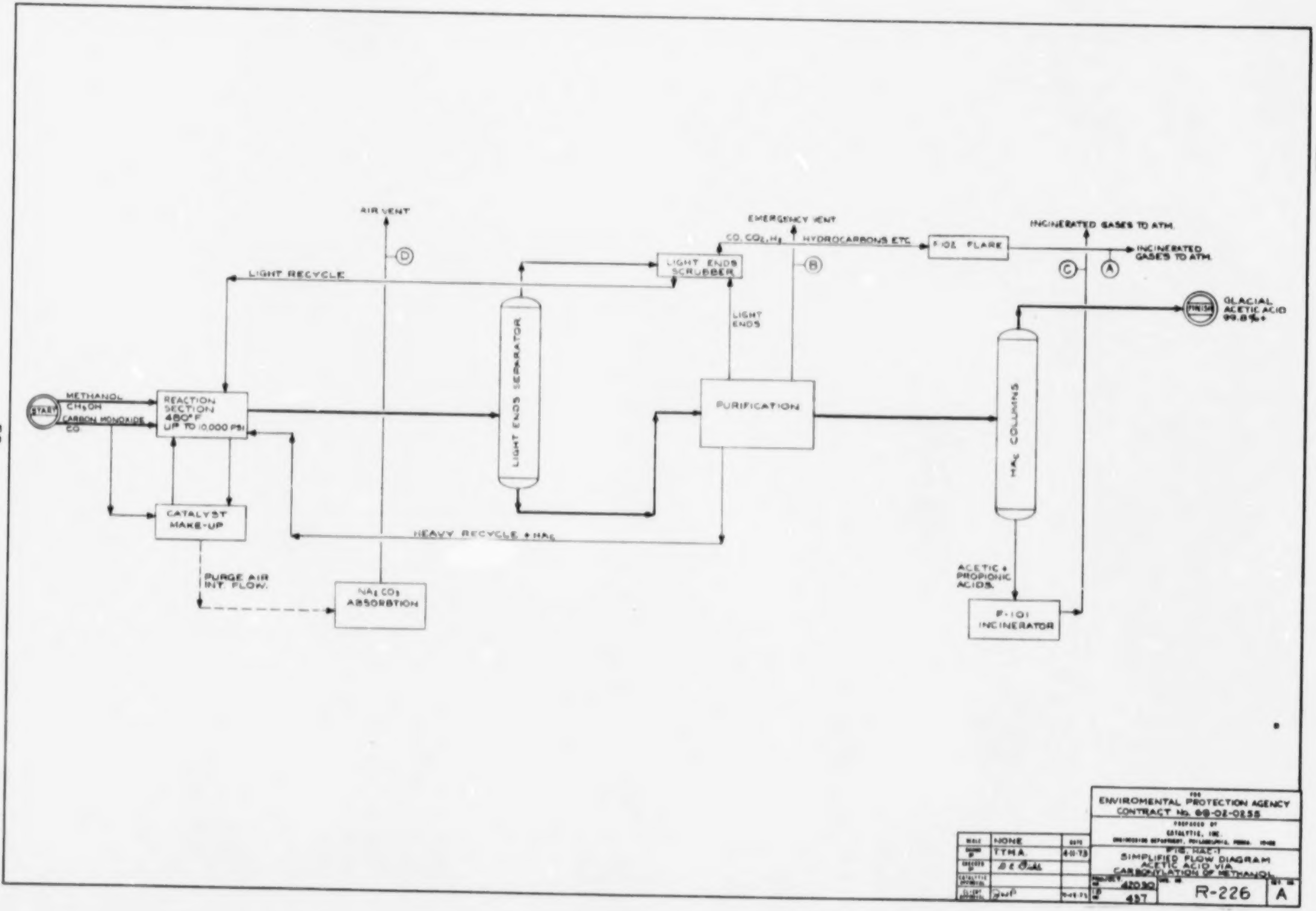

START
METHANOL
CH₃OH
CARBON MONOXIDE
CO
REACTION SECTION 480°F UP TO 10,000 PSI
CATALYST MAKE-UP
PURGE AIR INT. FLOW.
NA₂CO₃ ABSORBTION
AIR VENT
D
LIGHT RECYCLE
LIGHT ENDS SEPARATOR
HEAVY RECYCLE + HAc
LIGHT ENDS SCRUBBER
CO, CO₂, H₂
EMERGENCY VENT
HYDROCARBONS ETC.
B
LIGHT ENDS
PURIFICATION
F-102 FLARE
INCINERATED GASES TO ATM.
INCINERATED GASES TO ATM.
C
A
HAc COLUMNS
FINISH
GLACIAL ACETIC ACID 99.8%+
ACETIC + PROPIONIC ACIDS.
F-101 INCINERATOR
FOR ENVIROMENTAL PROTECTION AGENCY CONTRACT No. 68-02-0255
PREPARED BY CATALYTIC, INC.
FIG. HAC-1
SIMPLIFIED FLOW DIAGRAM ACETIC ACID VIA CARBONYLATION OF METHANOL
NONE
TTMA
4-11-73
42030
437
R-226
A

TABLE HAC-I
ACETIC ACID FROM METHANOL AND CO

Of the two respondent questionnaires, only one had sufficient data to construct a material balance. The other had apparently a large excess of snythesis gas, only a portion of which was used in the process and the excess flared.

Balance - in lb./lb. acetic acid

Material In			Lb./Lb.
Raw CO -	CO		0.512
	N_2		0.004
	CH_4		0.004
CH_3OH			0.540
		Total In	1.060

Material Out			
Acetic Acid -	CH_3COOH		1.000
Heavy Liquids	(CH_3COOH		0.003
(Mixed)	(CH_3CH_2COOH		0.001
Tail Gas -	CO		0.040
	CO_2		0.013
	H_2		0.001
	Others		0.001
Unaccounted for			0.001
		Total Out	1.060

TABLE HAC-II
ACETIC ACID FROM METHANOL AND CO

Very little data are available for construction of a detailed heat balance for this process. Literature reports the liquid phase reaction as mildly exothermic with only preheaters required to bring the reactants up to temperature.

HEAT IN	BTU/Lbs. HAC
Preheat reactants to 480° F	213
Exothermic heat of reaction	984*
	1,197
HEAT OUT	
Enthalpy of products leaving reactor	1.197

60° temperature base and no external losses assumed.

*Literature reports heat release of 1.9 x 10^6 BTU/ton acid vs calculated 1.968 x 10^6 BTU/ton HAC (984 BTU/lb. HAC).

TABLE HAC-III
NATIONAL EMISSIONS INVENTORY
ACETIC ACID FROM METHANOL AND CO

Plant EPA Code No.		2-3			2-6	
Capacity, Tons HAC/Yr.		50,000			150,000	
Range of Production, % of Max		0			0	
Emissions to Atmosphere - Stream	(A)	(B)	(C)	(A)	(B)	(C)
Flow - Lbs./Hr.	36,480 (1)		2,209 (1)	3,085 (1)	Nil	297 (1)
Flow Characteristic	Continuous		Continuous	Continuous	Open only in emergency	Continuous
Composition, Ton/Ton HAC	N. A.		N. A.	N. A.		N. A.
HAC					1.000	
Vent Stacks						
Number	1	1	1	1	1	N. A.
Height - feet	100	100	10	199	10	
Diameter - Inches	48	4	96	16	8	
Exit Gas Temp.	3600° F	90° F	3400° F	N. A.	Ambient	
SCFM/Stack	7300 (1)		426 (1)	475	1090	
Emission Control Devices						
Flare/Incinerator	Incinerator		Incinerator	Flare	None	Incinerator
Absorber/Scrubber						
Condenser/F. O. Drum						
Other						
Analysis						
Date or Frequency of Sampling	Never		Spot		Never	N. A.
Sample Tap Location	None		?		None	
Type of Analysis	None		None		None	
Odor Problem	None		No	Yes		
Summary of Air Pollutants	No Data		No Data			No data
Hydrocarbons, Ton/Ton HAC					0.0000	
Aerosols and Particulates, Ton/Ton HAC					1.0000	
NO_x, Ton/Ton HAC					0.0000	
SO_x, Ton/Ton HAC					0.0000	
CO , Ton/Ton HAC					0.0000	

(1) Calculations from composition and lbs./hr. of feed to incinerator or flare, an estimate.

TABLE HAC-IV

CATALOG OF EMISSION CONTROL DEVICES

ACETIC ACID FROM METHANOL AND CO

INCINERATION DEVICES				
EPA Code for plant using	2-3	2-3	2-6	2-6
Flow Diagram (Fig. HAC-1) Stream I. D.	(C)	(A)	(C)	(A)
Device I. D. No.	F-101	F-102	F-101	F-102
Type of Compound Incinerated	Mixed Organic Acids	Hydrocarbons & Organic Gases	Mixed Organic Acids	Hydrocarbons & Organic Gases
Type of Device	Incinerator	Incinerator	Incinerator	Flare
Material Incinerated, SCFM (lb./hr.)	(1020)	7000	(137)	475
Auxiliary Fuel Req'd. (fuel, pilot)				
Type	Natural gas	None	?	?
Rate, BTU/hr.				
Device or Stack Height, ft.	10	100	No Data	199
Installed Cost - Mat'l. & Labor - $	210,000	100,000		No Data
Installed Cost based on "year" dollars	1972	1965		
Installed Cost, ¢/lb. Acetic Acid/Yr	0.21	0.10		
Operating Cost Annual - $ (1972)	28,000	4,000		
Operating Cost, ¢/lb. Acetic Acid	0.028	.004		
Efficiency - % - CCR (1)	No Data	No Data	No Data	No Data
Efficiency - % - SERR (1)	No Data	No Data		

ABSORBER/SCRUBBERS	
EPA Code No. for plant using	2-6
Flow Diagram (Fig. HAC-1) Stream I. D.	(D)
Control of	Iodine Vapor
Scrubbing/Absorbing Liquid	Sodium Carbonate
Type	Static bed
Scrubbing/Absorbing Liquid Rate - GPM	175 gal.-static
Operating Temp., °F	Ambient
Gas Rate - SCFM	13 (1)
T-T Height, Feet	6
Diameter, Feet	2.5
Washed gases to stack	Yes
Stack Height - Ft	?
Stack Diameter - Inches	?
Installed Cost - Mat'l & Labor - $	10,000
Installed Cost based on "year" dollars	1970
Installed Cost, ¢/lb. Acetic Acid/Yr	0.003
Operating Cost - Annual - (1972)	$2,625
Value of Recovered Product, $/Yr	0
Net Operating Cost - ¢/lb. Acetic Acid	0.0009
Efficiency - % - SE (1)	100
Efficiency - % - SERR (1)	100

(1) Average flow is intermittent at 1090 SCFM for 2 hrs./week

TABLE HAC-IV
CATALOG OF EMISSION CONTROL DEVICES
NOTES

1. Incinerators and Flares. No data on combusted gases given. There are no nitrogen or sulfur compounds in the gases and complete combustion should give only CO_2 and water.

2. Absorber is for recovery of iodine vapors from catalyst preparation and activation section. Flow is intermittent. Recovery of I_2 is given as 100%. Therefore, the SE and SERR based on iodine are 100%. Effluent gas to atmosphere is air only.

3. See Appendix V for definition and explanation.

TABLE HAC-V
NUMBER OF NEW PLANTS BY 1980
ACETIC ACID

Process	Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand* 1980	Capacity 1980	Capacity** to be Added	Economic Plant Size	Number of New Units
Methanol	400	0	400	4,000	1,800	1,400	400	4
Acetaldehyde	875	100	775		2,015	1,240	400	3
Butane	1,000	500	500		500	0		
Others	285	100	185		185	0		
	2,560	700	1,860		4,500			

NOTE: All capacities in MM lbs./year.

*From Final Report prepared by Processes Research, Inc., August 15, 1971.
**Assumes 50 - 55% of new capacity will be by methanol process.

TABLE HAC-VI
EMISSION SOURCE SUMMARY
TON/TON ACETIC ACID

Emission	Source		Total
	Purification Section	Acid Recovery	
Hydrocarbons			
Particulates & Aerosols			
NO_x	- See Below -		0.00003
SO_x			
CO			

Note:

All waste gas streams leaving this process are flared or incinerated. No data on combusted gases are available. However, these gases contain no NO_x or SO_x or particulates and if incinerated properly should give only CO_2 and H_2O as off gas, except about 20 - 40 ppm of NO_x from atmospheric nitrogen, as indicated in the total column.

TABLE HAC-VII
WEIGHTED EMISSION RATES

Chemical Acetic Acid

Process Carbonylation of Methanol

Increased Capacity by 1980 1400 MM lbs./year

Pollutant	Emissions, Lb./Lb.	Increased Emissions MM Lb./Year	Weighting Factor	Weighted Emissions MM Lb./Year
Hydrocarbons	0*	0	80	0
Aerosols & Particulates	0	0	60	0
NO_x	0.00003	0.042	40	2
SO_x	0	0	20	0
CO	0*	0	1	0

**Significant Emission Index = 2

---

*In lieu of any data to the contrary, complete combustion of the vent gases to CO_2 and H_2O assumed.
**See Appendix IV for explanation.

Acetic Acid via Butane

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III.	Plant Emissions	ACA-3
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V.	Significance of Pollution	ACA-7
VI.	Acetic Acid Producers	ACA-8

List of Illustrations and Tables

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Gross Heat Balance	Table ACA-II
Emission Inventory	Table ACA-III
Catalog of Emission Control Devices	Table ACA-IV
Number of New Plants by 1980	Table ACA-V
Emission Source Summary	Table ACA-VI
Weighted Emission Rates	Table ACA-VII

I. Introduction

Acetic acid is an important chemical used to produce acetic anhydride for cellulose acetate, vinyl acetate monomer for vinyl polymer, acetate esters for use as commercial solvents and chloroacetic acid for use in the leather and textiles industry. The manufacture of cellulose acetate and vinyl acetate monomer account for 44% and 31% of the acetic acid produced.

Acetic acid was first produced commercially by wood distillation. A concerted effort was made during World War I to make synthetic acetic acid because of its use in acetone synthesis. Today, almost all acetic acid is made by synthetic methods. The major routes are oxidation of n-butane, acetaldehyde oxidation and carbonylation of methanol. The first two processes account for 44% and 32% of the acetic acid capacity, respectively. The methanol carbonylation process is new and growth is expected in that area.

The oxidation of butane is used in two large acetic acid installations. Large quantities of by-products are produced by the process, the more useful of which are recovered. The economic success of such a plant is tied to a source of cheap butane and a high market value for by-products.

Acetic acid production is expected to grow to 4.5 billion lbs./yr.* by 1980, which is an increase of about 2 billion lbs./yr. Because butane has become more useful for other purposes and by-product formation is undesirable, future plants are expected to be built using either acetaldehyde oxidation or methanol carbonylation process.

Emissions from a butane oxidation plant can best be described as moderate. Since no growth is expected, however, annual emissions are not significant.

NOTE: This report is based on the data supplied by one respondent and information found in literature.

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*More recent estimates indicate that growth may be to 3.2 billion lbs./year by 1980, or only about 1 billion lbs./year increased capacity.

II. Process Description

(See Figure ACA-1)

The commercial oxidation of n-butane produces acetic acid along with a large number of by-products. Some of the useful by-products which are usually recovered and sold or used in captive processes include ethyl acetate, ethanol, methyl-ethyl ketone, formic acid and propionic acid. Product and by-product separation is extremely difficult because azeotropes are formed between many of the components and a large percentage of the capital and operating costs are tied up in the recovery area. The large number of by-products produced by butane oxidation (up to 70 components could be present in the reactor effluent stream) are the chief drawback to the process.

The oxidation of butane is carried out in recycle reactors due to low butane conversion. Typical reaction conditions described for a plant built by Chemische Werke Huls in Germany are as follows: oxidation is carried out in stainless steel towers at a temperature of 170 - 200° C and a pressure of 65 atmospheres. The reaction takes place in the presence of a large excess of reaction products and is considered a liquid phase reaction even though butane is above its critical temperature.

There is a considerable heat of reaction, 9,000 BTU/lb. butane oxidized. which must be removed mainly by evaporation of products and feed preheating. Oxidation can be carried out using air or oxygen. If air is used nitrogen must be removed from the system. Reaction products are separated from unreacted butane and combustion products such as carbon dioxide, carbon monoxide. etc. Butane is recycled, CO_2, CO and some hydrocarbons are vented and/or flared and the crude mixutre of products and by-products is sent to the purification system.

There are many schemes to carry out the difficult purification steps necessary. The following is a general description of a typical process. In the first step a crude separation is made between alcohols, acetates, aldehydes, ketones & light components and acids plus acid residues. The alcohols, acetates, etc., undergo another distillation whereby the heavy components, C_4's, are removed to incineration, the light solvents including acetone and methyl acetate are partially recycled to the reactor with the rest being burned, and the useful by-products, ethyl acetate, methyl ethyl ketone and ethanol are sent to further purification. Ethyl acetate is usually recovered and refined first, followed by ethanol and finally the ketone. The purification of these components involves either extractive distillation or azeotrope breakers or both.

The acids and residues passing from the bottoms of the crude separation column are sent to another column for removal of heavy residues, which are burned, and water which is sent to treatment. The mixture of acids leaving the column goes to further azeotropic distillation steps where the acids are separated and purified. Formic acid is recovered and purified first followed by acetic acid and then propionic acid.

Large amounts of liquid waste products (about .4 lb./lb. acetic acid) are produced by the process and they are burned in boilers to recover heat. The aqueous waste is usually sent to treatment.

III. Plant Emissions

A. Continuous Air Emissions

1. Reactor Section Emissions

The respondent shows a large number of streams outletting from the process section described as "stripping recycle reactors". To avoid possible inaccuracies it seemed wise to assign these streams to the general category "reaction section" and not attempt to guess the individual sources from which they originate. Emissions to the atmosphere from this section are described below without further clarification.

a. Flare Stack Emissions

Hydrocarbon liquids and gases from each of the two reactor sections are burned in a flare prior to release to the atmosphere. The liquid stream consists of 75 - 100 lbs./hr. of all types of acids, alcohols, acetates and ketones. The gaseous stream contains mainly carbon dioxide (approximately 80 wt. %) with smaller amounts of butane, ethane, methane and inert argon. Since no sulfur or nitrogen compounds are present in the incinerated streams and no smoke or odor is reported by the respondent it is assumed that nearly complete combustion takes place and the only emissions are carbon dioxide, water and traces of NO_x and unburned hydrocarbons.

b. Vent No. 1

One or two streams composed mainly of carbon dioxide with large quantities of butane and smaller amounts of ethane and methane are vented to the atmosphere from each of the reactor sections. Carbon monoxide, nitrogen and argon are also present in the stream. Total hydrocarbon emissions for all vents in this category are .03824 lbs./lb. acetic acid. Carbon monoxide emissions are .01354 lbs./lb. acetic acid from this source.

c. Vent No. 2

Each reactor section has a small vent (.21 SCFM) for light gases. Small amounts of hydrocarbons (.00001 lbs./lb. acetic acid) are emitted.

2. Liquid Waste Boiler - Flue Gas

The large quantity of organic liquid waste described in Section III-C-1 of this report, is burned in boilers. No sulfur or nitrogen is present in any of the components so combustion is assumed to be complete. NO_x composition is estimated to be 30 PPM which is .00004 lbs./lb. acetic acid for the quantity of liquid burned.

3. Storage Tank Losses

The respondent estimates that .00087 lbs. of product and by-product per lb. of acetic acid, is lost due to storage tank venting.

B. Intermittent Air Emissions

1. Topping Column and Crude Separation Column Venturi Scrubbers - Accumulator Relief Vent

Both the crude separation column and the topping column have two Venturi scrubbers to absorb organic vapors, which are assumed to originate from the reflux accumulators. The accumulator on the scrubber exhaust is covered with a methane pad. Infrequent pressure release allows methane along with some acetone, methyl acetate, acetaldehyde and other light alcohols, acetates, aldehydes and ketones to enter the atmosphere. The total quantity vented is considered insignificant on a yearly basis.

2. Purification Section Pressure Relief Vents

Small amounts of methane along with hydrocarbons are released by pressure relief on columns in the purification section. The total amount emitted to the atmosphere is described by the respondent as small.

C. Continuous Liquid Wastes

1. Liquid Waste to Incineration

Large quantities of unrecovered by-products produced by the process are burned. The source and composition of these streams is described below.

a. Acid Purification Section

Approximately 19,000 lbs./hr. of C_1 - C_4 acids and water are released from the acid purification section to boilers or incinerators.

b. Topping Column Bottoms

About 6,000 lbs./hr. of butyl esters and alcohols exit from the topping column to boilers.

c. Light Solvents from Topping Column

Unrecycled acetone, acetaldehyde, methyl acetate, etc., are burned.

2. Waste Water

An estimated flow of 200 GPM of waste water from the process is treated in an anaerobic lagoon.

D. Solid Waste

Acid residue is burned in boilers.

E. Odor Problem

The respondent reports that odors of acetone, acetic acid and methyl acetate are infrequently detectable off of the plant property.

F. Fugitive Emissions

No other sources of emissions were mentioned although losses due to leaks and spills probably do occur.

IV. Emission Control

The emission control devices that have been reported as being employed by the respondent are summarily described in Table IV of this report. An efficiency has been assigned each device wherever data sufficient to calculate it have been made available. Three types of efficiencies have been calculated.*

(1) "CCR" - Completeness of Combustion Rating

$$\text{CCR} = \frac{\text{lbs. of } O_2 \text{ reacting (with pollutant in device feed)}}{\text{lbs. of } O_2 \text{ that theoretically could react}} \times 100$$

(2) "SE" - Specific Efficiency

$$\text{SE} = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

(3) "SERR" - Significance of Emission Reduction Rating

$$\text{SERR} = \frac{(\text{pollutant} \times \text{weighting factor})\text{in} - (\text{pollutant} \times \text{weighting factor})\text{out}}{(\text{pollutant} \times \text{weighting factor*})\text{in}} \times 100$$

*Weighting factor same as Table VII weighting factor.

Emission Control Devices Employed

Flares (with steam rings for emergency smokeless operation)

The respondent claims flares are smokeless so complete combustion is assumed to the extent possible with flares.

Venturi Scrubbers

Since the only emission from the scrubbers is infrequent pad gas vents the "SE" and "SERR" efficiencies are near 100%.

---

*For complete description, see Appendix V of this report.

V. Significance of Pollution

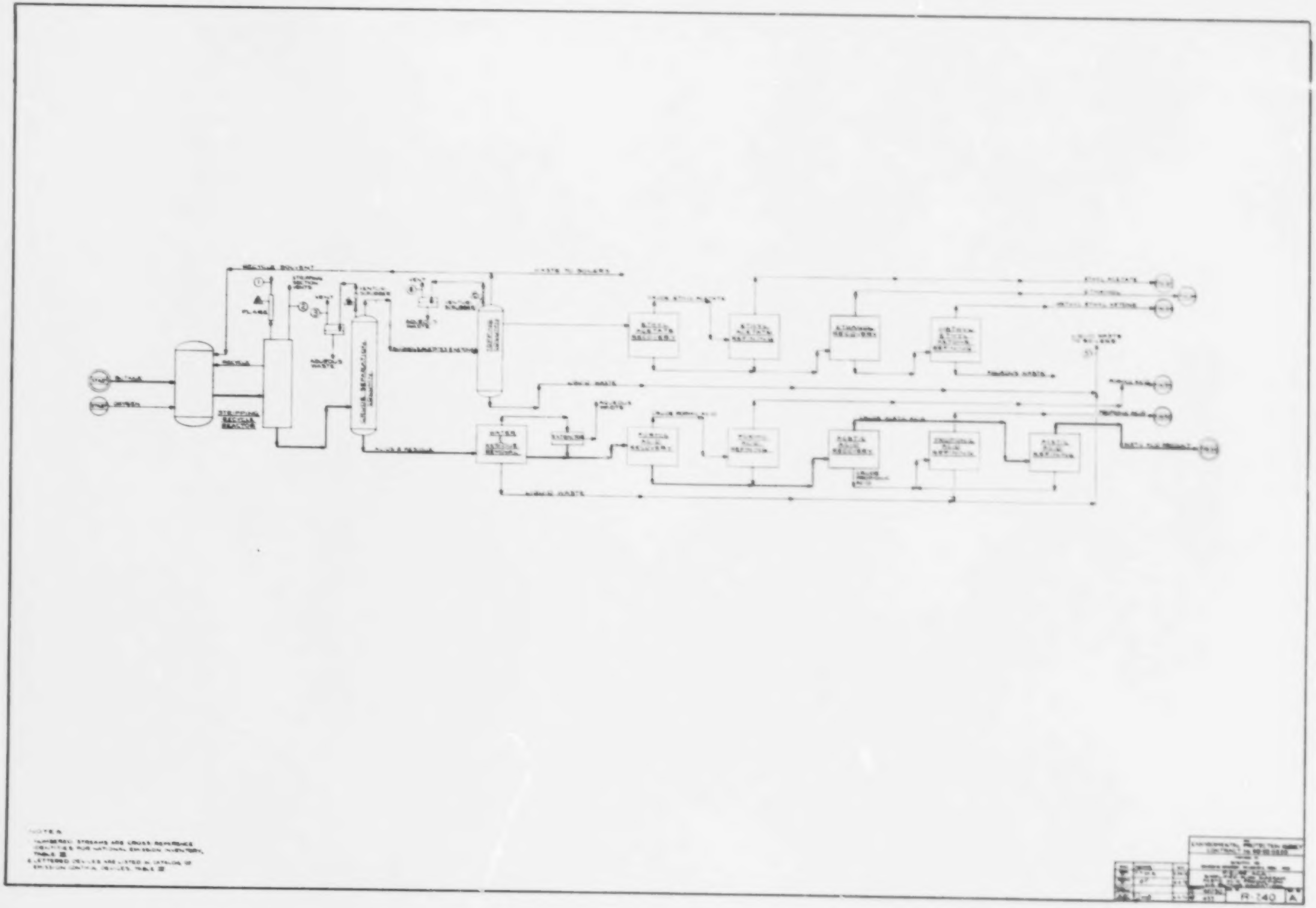
It is recommended that no in-depth study be made of the butane oxidation process for acetic acid. This conclusion is drawn because no growth is expected in the process between now and 1980. The reasons for this are as follows:

1. Butane is becoming important for other purposes.
2. The methanol carbonylation process is growing in favor.
3. Large quantities of by-products are undesirable.

Since no new capacity is anticipated, the Significant Emissions Index (SEI) for the oxidation of butane route to acetic acid is zero. For explanation of SEI, see Appendix IV of this report.

VI. Synthetic Acetic Acid Producers

Producer	Location	Butane Oxidation	Acetaldehyde	Methanol & CO	By-Product
Borden Inc.	Geismar, La.			100	
Celanese Corp.	Bayport, Texas		300		
	Bishop, Texas		150		
	Pampa, Texas	500			
Eastman Kodak	Kingsport, Tenn.		325		
FMC Corp. (peracetic acid)	Bayport, Texas				45
Monsanto Co.	Texas City, Texas			300	
Publicker Ind., Inc.	Phila., Pa.				80
Union Carbide (peracetic acid)	Brownsville, Texas	520			
	Taft, La.				90
	Texas City, Texas		100		
	Total -	1,020	875	400	210
	Percentage Total -	41	35	16	8


BUTANE
OXYGEN
RECYCLE SOLVENT
FLARE
VENT
AQUEOUS WASTE
WASTE TO BOILERS
ETHYL ACETATE
ETHANOL
METHYL ETHYL KETONE
LIQUID WASTE
ACETIC ACID PRODUCT
R-140
A

NOTES:
1. NUMBERED STREAMS AND DEVICES REFERENCE QUANTITIES FOR NATIONAL EMISSION INVENTORY, TABLE [illegible]
2. LETTERED DEVICES ARE LISTED IN CATALOG OF EMISSION CONTROL DEVICES, TABLE [illegible]

TABLE ACA-I
MATERIAL BALANCE
ACETIC ACID
VIA
BUTANE OXIDATION

MATERIAL IN

BUTANE

1)	n-butane	1.130
2)	iso-butane	.017
3)	lights and heavies	.006

OXYGEN

1)	oxygen	1.578
2)	nitrogen	.097
3)	argon	.003

Total In - 2.831 lb./lb. 99% acetic acid

MATERIAL OUT (LB./LB. ACETIC ACID)

99% acetic acid	1.000
98% formic acid	.030
95% propionic acid	.003
99.5% methyl-ethyl ketone	.159
85% ethanol	.031
99% ethyl acetate	.119
waste liquid and gases	1.489

Total Out - 2.831 lb./lb.
99% acetic acid

TABLE ACA-II
GROSS HEAT BALANCE
ACETIC ACID
VIA
BUTANE OXIDATION

There is insufficient data available for a complete energy balance on this process.

Heat of Reaction

9,000 BTU/lb. butane oxidized*

---

*1) Includes all products and by-products.

2) Reported for Chemische Werke Huls' n-butane oxidation process in Chemistry and Industry, May 28, 1966. Different relative amounts of products and by-products are produced by this process than were reported by the only respondent in the study, so the heat of reaction might vary somewhat.

TABLE ACA-III
NATIONAL EMISSIONS INVENTORY
ACETIC ACID
VIA
BUTANE OXIDATION

Page 1 of 3

EPA Code No.	2-1				
Capacity - Tons of Acetic Acid	260,000				
Production - Tons of Acetic Acid	260,000				
Emissions to Atmosphere					
Stream No.	2	2	2	2	2
Stream	Reactor I Section Vent 1	Reactor I Section Vent 2	Reactor II Section Vent 1A	Reactor II Section Vent 1B	Reactor III Section Vent 2
Flow - Lbs./Hr.	14,065	1.4	8005	6720	1.4
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr.					
Composition					
Ethane	.00367		00149	00134	
Methane	.00245		00075	00185	
Butane	.01743		00136	00274	
Carbon Dioxide	.15289	.00001	.10956	05790	00001
Carbon Monoxide	.00685	+		00669	+
Oxygen		+			+
Nitrogen	.00499	+	00230	.00750	+
Nitrogen Oxides					
Water					
Argon	.02076	+	00185	02120	+
Hydrocarbons (assorted)	~ .00409	00001	00348	~ 00267	00001
Acetone					
Acetaldehyde					
Methyl Acetate					
Analysis	Yes	Yes	Yes	Yes	Yes
Sample Tap Location	Side of Units	None	Side of Unit	Side of Unit	None
Date or Frequency of Sampling	3 times a week	On request	3 times a week	3 times a week	On request
Type of Analysis	Mass Spectrometer	Mass Spectrometer	Mass Spectrometer	Mass Spectrometer	Mass Spectrometer
Odor Problem	No	No	No	No	No
Vent Stacks	Yes	Yes	Yes	Yes	Yes
Number	1	1	1	1	1
Height - Ft.	90	20	100	100	17
Diameter - Inches	10	2	10	10	5
Temp. - F°	100	80	90	86	80
Flow Rate - SCFM per stack	2023	.2	1,154	1,043	2
Emission Control Device	No	No	No	No	No
Type - Incinerator					
Scrubber					
Summary of Emissions					
Total Hydrocarbon Emissions - Ton/Ton of Acetic Acid					
Total Particulate Emissions - Ton/Ton of Acetic Acid					
Total NO_x Emissions - Ton/Ton of Acetic Acid					
Total SO_x Emissions - Ton/Ton of Acetic Acid					
Total CO Emissions - Ton/Ton of Acetic Acid					

Continued

TABLE ACA-III
NATIONAL EMISSIONS INVENTORY
ACETIC ACID
VIA
BUTANE OXIDATION

Page 2 of 3

EPA Code No.	2-1			
Capacity - Tons of Acetic Acid	260,000			
Production - Tons of Acetic Acid	260,000			
Emissions to Atmosphere				
Stream No.	1A	1B	3A	
Stream	Flare Stack Emissions Reactor Section I Flare (1)	Flare Stack Emissions Reactor Section II Flare (3)	Topping Column Venturi Scrubber Vent (4)	
Flow - Lbs./Hr.	3380 (2)	~6700 (2)	>0	
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Intermittent	
If Intermittent - Hrs./Yr.			Not Specified	
Composition				
Ethane				
Methane			+	
Butane				
Carbon Dioxide	.03875	.08691		
Carbon Monoxide				
Oxygen				
Nitrogen				
Nitrogen Oxides	Negligible	Negligible		
Water	.01245	.01433		
Argon	.00041	.00087		
Hydrocarbons (assorted)				
Acetone			+	
Acetaldehyde			+	
Methyl Acetate			+	
Analysis	None	None	None	
Sample Tap Location				
Date or Frequency of Sampling				
Type of Analysis	(2)	(2)		
Odor Problem	No	No	Yes	
Vent Stacks	Yes	Yes	Yes	
Number	1	1	2	
Height - Ft.	210	210	58	42
Diameter - Inches	24	24	3	6
Temp. - F°	Unknown	Unknown	90	86
Flow Rate - SCFM per stack	660	1150		
Emission Control Devices	Yes	Yes		
Type - Incinerator				
Flare	Yes	Yes		
Scrubber			Yes	
Summary of Emissions				
Total Hydrocarbon Emissions - Ton/Ton of Acetic Acid		Continued		
Total Particulates and Aerosols - Ton/Ton of Acetic Acid				
Total NO_x - Ton/Ton of Acetic Acid				
Total SO_x - Ton/Ton of Acetic Acid				
Total CO - Ton/Ton of Acetic Acid				

(1) Approximately 2825 lbs./hr. of light hydrocarbons and 75 lbs./hr. of liquid alcohols, acids and ketones are incinerated in this flare.

(2) Combustion products estimated by Houdry assuming complete conversion to CO_2 and H_2O and 30 PPM NO_x formation.

(3) Approximately 3610 lbs./hr. of light hydrocarbons and 100 lbs./hr. of liquid alcohols, acids and ketones are incinerated in this flare

(4) Infrequent pressure release of methane pad.

(5) Mostly methane.

TABLE AC6-III
NATIONAL EMISSIONS INVENTORY
ACETIC ACID
VIA
BUTANE OXIDATION

EPA Code No.	2-1			
Capacity - Tons of Acetic Acid	260,000			
Production - Tons of Acetic Acid	260,000			
Emissions to Atmosphere				
Stream No.	4	5		
Stream	Crude Separation Column, Venturi Scrubber Vent (4)	Flue Gas Liquid Waste Boilers	Storage Tank Vents	Purification Relief Valve
Flow - Lbs./Hr.	>0	49,267 (2)	57.8	>0
Flow Characteristic - Continuous or Intermittent	Intermittent	Continuous		Intermittent
if Intermittent - Hrs./Yr.	Not Specified			Not Specified
Composition				
Ethane	+			+
Methane	(5)			
Butane				
Carbon Dioxide		46192		
Carbon Monoxide				
Oxygen				
Nitrogen				
Nitrogen Oxides		00004		
Water		26356		
Argon				
Hydrocarbons (assorted)			.00087	+
Acetone	+			
Acetaldehyde	+			
Methyl Acetate	+			
Analysis	None	None	None	None
Sample Tap Location				
Date or Frequency of Sampling				
Type of Analysis		(2)	Calculated	
Odor Problem	Yes	No	No	No
Vent Stacks	Yes	Not Specified		No
Number	2			
Height - Ft.	55 55			
Diameter - Inches	3 3			
Temp. - F°	98 98			
Flow Rate - SCFM per stack				
Emission Control Devices	Yes	No	No	No
Type - Incinerator				
Flare				
Scrubber	Yes			
Summary of Emissions				
Total Hydrocarbon Emissions - Ton/Ton of Acetic Acid		03911		
Total Particulate and Aerosols - Ton/Ton of Acetic Acid		0		
Total NO_x - Ton/Ton of Acetic Acid		00004		
Total SO_x - Ton/Ton of Acetic Acid		0		
Total CO - Ton/Ton of Acetic Acid		01356		

(1) Approximately 2825 lbs./hr. of light hydrocarbons and 75 lbs./hr. of liquid alcohols, acids and ketones are incinerated in this flare.
(2) Combustion products estimated by Houdry assuming complete conversion to CO_2 and H_2O, and 30 PPM NO_x formation.
(3) Approximately 3610 lbs./hr. of light hydrocarbons and 100 lbs./hr. of liquid alcohols, acids and ketones are incinerated in this flare.
(4) Infrequent pressure release of methane pad
(5) Mostly methane.

TABLE ACA-IV
CATALOG OF EMISSION CONTROL DEVICES
ACETIC ACID
VIA
BUTANE OXIDATION

FLARE

EPA Code No. for plant using	2-1		2-1
Flow Diagram (Fig. ACA-I) Stream I. D.	A_1		A_2
Device I. D. No.	FL-I		FL-II
Types of Compounds Flared	Assorted HC Liquids & Vapors		Assorted HC Liquids & Vapors
Amount Flared - lbs./hr.	2790		3450
Device or Stack Height - Ft.	210		210
Stack Diameter @ Tip - Inches	24		24
Installed Cost - Mat'l. & Labor - $	84,760		84,760
Installed Cost - Mat'l. & Labor - ¢/lb. Acetic Acid	.016		.016
Installed Cost - based on - "year" - $	34,760 - 1971 50,000 - 1961		34,760 - 1971 50,000 - 1964
Operating Cost - Annual - (1972)		16,560	
Operating Cost Annual - ¢/lb. Acetic Acid		.003	
Efficiency - CCR - %		Near 100%	
Efficiency - SERR - %		Near 100%	

SCRUBBERS

EPA Code No. for plant using	2-1	2-1	
Stream I. D. No.	B	B	
Device I. D. No.	SC-I & SC-II	SC-III & SC-IV	
Control Emission of	Acetaldehyde, Acetone, Methyl Acetate	Acetaldehyde, Acetone, Methyl Acetate	
Scrubbing Liquid	Water	Water	
Type - Venturi	Yes	Yes	
Absorber			
Scrubbing Liquid Rate - GPM	9.2 each		
Design Temp. - F°			
Gas Rate - SCFM (lb./hr.)			
Washed Gases to Stack	Yes	Yes	
Stack Height - Ft.	55 each	58	42
Stack Diameter - Inches	3 each	3	6
Installed Cost - Mat'l. & Labor - $	4,000	2,000	2,000
Installed Cost - ¢/lb. of Acetic Acid	.0008	.0004	.0004
Installed Cost - based on - "year" - $	1964	1964	1968
Operating Cost - Annual - (1972)	200	200	
Value of Recovered Product - $/Yr.	0	0	
Net Operating Cost - Annual - $	200	200	
Net Operating Cost - ¢/lb. of Acetic Acid	.00004	.00004	
Efficiency - % - SE	99.9+	99.9+	
Efficiency - % - SERR	99.9+	99.9+	

TABLE ACA-V
NUMBER OF NEW PLANTS BY 1980
ACETIC ACID
VIA
BUTANE OXIDATION

Current (1) Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
1020	0	1020	1020	1020	0	300	0 (2)

(1) MM lbs./year.

(2) No new butane oxidation plants are expected to be built.

TABLE ACA-VI
EMISSION SOURCE SUMMARY
TON/TON OF ACETIC ACID

Emission	Source				Total
	Reactor Stripping Section	Liquid Waste Incineration	Venturi Scrubber and Purification Section Relief Valves	Tank Vents & Fugitive Emissions	
Hydrocarbons	.03824	0	Negligible	.00087	.03911
Particulates	0	0	0	0	0
NO_x	0	.00004	0	0	.00004
SO_x	0	0	0	0	0
CO	.01354	0	0	0	.01354

TABLE ACA-VII
WEIGHTED EMISSION RATES

Chemical Acetic Acid

Process Butane Oxidation

Increased Capacity by 1980 0

Pollutant	Emissions Lb./Lb.	Increased Emissions MM Lbs./Year	Weighting Factor	Weighted Emissions MM Lbs./Year
Hydrocarbons	.03911	0	80	0
Particulates	0	0	60	0
NO_x	.00004	0	40	0
SO_x	0	0	20	0
CO	.01354	0	1	0

Significant Emission Index = 0

Acetic Acid via Acetaldehyde

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I. Introduction

Acetic acid is an important chemical used to produce acetic anhydride for cellulose acetate, vinyl acetate monomer for vinyl polymer, acetate esters for use as commercial solvents and chloroacetic acid for use in the leather and textiles industries. The manufacture of cellulose acetate and vinyl acetate monomer account for 44% and 31%, respectively, of the acetic acid produced.

Acetic acid was first produced commercially by wood distillation. A concerted effort was made during World War I to make synthetic acetic acid because of its use in acetone synthesis. Today, almost all acetic acid is made by synthetic methods. The major routes are oxidation of n-butane, acetaldehyde oxidation and carbonylation of methanol. The first two processes account for 44% and 32%, respectively, of the acetic acid capacity. The methanol carbonylation process is new and growth is expected in that area.

It seems that in the future methanol carbonylation will become the most important process to manufacture acetic acid. How long this will take, however, is difficult to predict. In recent years both Hercules and Union Carbide have shut down their older acetaldehyde oxidation plants. On the other hand, Celanese built its new acetic acid plant at Clear Lake, Texas in 1970 using the acetaldehyde process. No definite conclusion can be drawn.

Only one questionnaire was received from plants producing acetic acid from acetaldehyde. The plant responding uses a combined feed of acetaldehyde and ethanol. Therefore, the emission data may or may not represent the acetaldehyde oxidation industry as a whole.*

The only source of emissions reported by the respondent is from the off-gas absorber vent. Emissions from this source could best be described as moderate.

*Subsequent to the completion of this report, a producer using only acetaldehyde as feed to the process reported that their Significant Emission Index was "less than 978.5".

II Process Description

Acetic acid can be produced commercially by direct oxidation of acetaldehyde. In a variation of the process, used by the only respondent to the questionnaire on acetaldehyde oxidation, ethanol is mixed with acetaldehyde and the two components are oxidized together. These processes are described below. (See Fig. ACE-1)

Acetaldehyde Oxidation

The continuous oxidation of acetaldehyde is generally carried out in the liquid phase using air or oxygen in the presence of either manganous or cobalt acetate. The acetate serves the purpose of decomposing any peracetic acid that forms. The reaction usually takes place with a large excess of the reaction product, acetic acid in the reactor vessel. Typical reaction conditions are 55 - 65° C at 70 - 75 PSI using air and 70 - 80° C and a pressure sufficient to keep acetaldehyde liquid using oxygen. Both a liquid and a gaseous stream exit from the reactor.

The gaseous stream is scrubbed many times, first with dilute acetic acid and then with refrigerated water to recover valuable acetic acid and acetaldehyde. Nitrogen along with carbon dioxide and unrecovered organics are vented to the atmosphere. The liquid reactor effluent contains mainly acetic acid, water and unreacted acetaldehyde. The acetaldehyde can be removed by either air stripping or distillation and is then recycled to the reactor. The dilute acetic acid is distilled to remove water and any impurities and is sent to storage.

Acetaldehyde - Ethanol Oxidation

Acetaldehyde and ethanol can be oxidized using air or oxygen in the liquid or vapor phase. The reactor effluent consists of a mixture of acetic acid, acetaldehyde, ethanol and ethyl acetate formed by the chemical combination of some acetic acid with ethanol. The liquid phase reaction is carried out in an acetic acid solution using a mixture of cobalt and chromium acetate as a catalyst. Fresh feed in the case of the only respondent to the questionnaire contains 77.5 wt. % acetaldehyde and 22.5 wt. % ethanol (92.5% solution). The ethanol and acetaldehyde are separated from acetic acid and are returned to the reactor as recycle. Ethyl acetate is distilled off and recovered as a by-product. Finally, acetic acid is refined with water being driven off overhead and glacial acetic acid recovered as product.

An overall material balance and information on heats of reaction can be found in Tables I and II, respectively.

III. Plant Emissions

A. Continuous Air Emissions

1. Absorber Vent

The emissions from this vent constitute the only major source of air pollution associated with the production of acetic acid by acetaldehyde-ethanol oxidation.

The vent stream is composed primarily of nitrogen. Smaller quantities of ethyl acetate, acetaldehyde, carbon dioxide, carbon monoxide, water and oxygen are also present. Plant 2-5, the only respondent, **reports** the following emissions from the two absorbers used in the process.

Component	Lbs./Lb. Acetic Acid
Acetaldehyde	.00481
Ethyl Acetate	.00502
Carbon Dioxide	.02089
Carbon Monoxide	.00202
Water	.00077
Oxygen	.04529
Nitrogen	1.26869

A more complete description of emissions can be found in Table III.

2. Storage Tank Losses

Ethanol storage tanks are covered with an inert gas pad, while dilute acetic acid storage tanks vent into the process. Glacial acetic acid is the only material which is allowed to vent directly to the atmosphere. Losses in the storage area are reported to be negligible.

B. Intermittent Air Emissions

No sources of intermittent air emissions were reported.

C. Continuous Liquid Waste

1. Waste Water

80 gal./min. of waste water is produced. The respondent reports that waste water is treated on-site.

D. Solid Wastes

No solid wastes are produced.

E. Odor

In general, this process does not appear to present an odor problem. No odors were reported detectable on-site or off-site.

F. Fugitive Emissions

Leaks due to pump seals are collected in the process. Other leaks are described as "very minor".

IV. Emission Control

The emission control devices that have been reported as being employed by the respondent are summarily described in Table IV of this report. Efficiencies have been assigned each device. Two types of efficiencies have been calculated.*

(1) "SE" - Specific Efficiency

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

(2) "SERR" - Significance of Emission Reduction Rating

$$SERR = \frac{(\text{pollutant} \times \text{weighting factor}^{*})\text{in} - (\text{pollutant} \times \text{weighting factor})\text{out}}{(\text{pollutant} \times \text{weighting factor})\text{in}} \times 100$$

*Weighting factor same as Table VII weighting factor.

Description of Emission Control Devices Employed

Absorbers

Two identical absorbers operating in paralled are employed by plant 2-5 to recover valuable product, by-product and recycle materials from the reaction off-gas prior to release to the atmosphere. Each absorber is divided into two sections. In the first section, incoming gases, which contain large amounts of acetic acid, ethanol, ethyl acetate and acetaldehyde are scrubbed with 5% acetic acid. In the second section, components are absorbed by water. Acetic acid and ethanol are completely removed by this operation. The efficiency of removal of acetaldehyde and ethyl acetate is 97.8% and 88.7%, respectively. Overall efficiency for all pollutants characterized by the "SERR" index is 98.6%.

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*For a more complete description of these efficiencies, see Appendix V.

V. Significance of Pollution

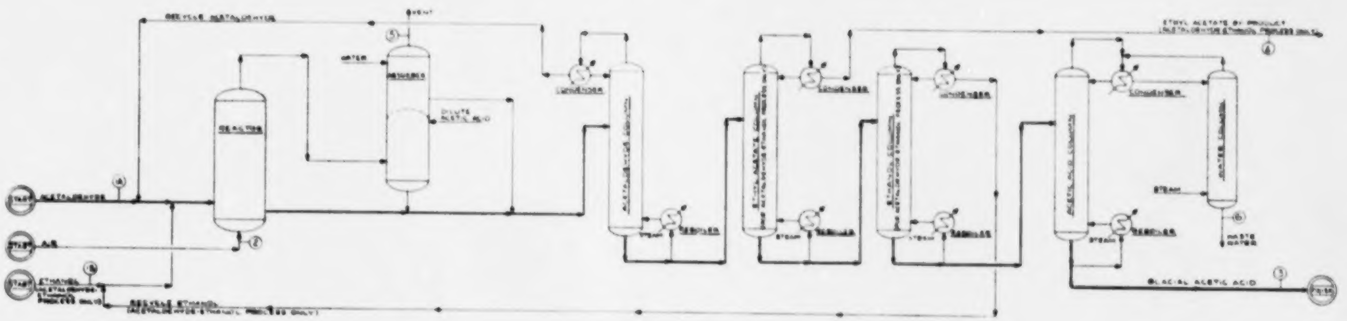
It is recommended that no in-depth study of the acetaldehyde oxidation process be made at this time. The reported emission data indicate that the quantity of pollutants released as air emissions is less for the subject process than for processes currently under in-depth study.

The methods outlined in Appendix IV of this report have been used to estimate the total weighted annual emissions from new plants. This work is summarized in Tables V, VI and VII. An accurate growth rate for the acetaldehyde process is difficult to estimate do to expected methanol carbonylation growth. Recent shutdowns as opposed to the opening of a new acetaldehyde plant by Celanese confuse the picture to an even greater extent. At this point it seems that the future acetic acid industry will turn to methanol carbonylation. How long this will take is difficult to predict.

On a weighted emission basis a Significant Emission Index of 978.5 has been calculated in Table VII. This is substantially lower than other processes which are being studied in-depth. Hence, the recommendation to exclude acetic acid by acetaldehyde oxidation from the in-depth portion of the work for this project.

VI. Synthetic Acetic Acid Producers

Company	Location	Butane Oxidation	Acetaldehyde	Methanol & CO	By-Product
Borden, Inc.	Geismar, La.			100	
Celanese Corporation	Bayport, Texas		300		
	Bishop, Texas		150		
	Pampa, Texas	500			
Eastman Kodak	Kingsport, Tenn.		325		
FMC Corporation (peracetic acid)	Bayport, Texas				45
Monsanto Company	Texas City, Texas			300	
Publicker Industries, Inc.	Philadelphia, Pa.				80
Union Carbide (peracetic acid)	Brownsville, Texas	520			
	Taft, La.				90
	Texas City, Texas		100		
	Total	1,020	875	400	210
	% Total	41	35	16	8


START ACETALDEHYDE
START AIR
START ETHANOL (ACETALDEHYDE-ETHANOL PROCESS ONLY)
RECYCLE ACETALDEHYDE
REACTOR
VENT
WATER
ABSORBER
DILUTE ACETIC ACID
CONDENSER
ACETALDEHYDE COLUMN
REBOILER
STEAM
ETHYL ACETATE COLUMN (FOR ACETALDEHYDE-ETHANOL PROCESS ONLY)
ETHANOL COLUMN (FOR ACETALDEHYDE-ETHANOL PROCESS ONLY)
ACETIC ACID COLUMN
WATER COLUMN
WASTE WATER
ETHYL ACETATE BY-PRODUCT (ACETALDEHYDE-ETHANOL PROCESS ONLY)
RECYCLE ETHANOL (ACETALDEHYDE-ETHANOL PROCESS ONLY)
GLACIAL ACETIC ACID
FINISH
2
3
4
5
6

NOTES:
1. NUMBERED STREAMS ARE CROSS REFERENCE IDENTITIES FOR MATERIAL BALANCE - TABLE 1

ENVIRONMENTAL PROTECTION AGENCY
CONTRACT No. [illegible]

R-238 A

TABLE ACE-I
MATERIAL BALANCE
ACETIC ACID
VIA
ACETALDEHYDE OXIDATION
WITH
ACETALDEHYDE-ETHANOL FEED

T/T ACETIC ACID

	IN		OUT			
Stream I. D. No.	1	2	3	4	5	6
Stream	Fresh Feed	Air	Product	By-Product	Off-Gas	Waste Water
Component						
Acetaldehyde	.6102				.0048	
Ethanol - 92.5%						
1) Ethanol	.1667					
2) Water	.0136				.0006	.0777
Air						
1) Oxygen		.3886			.0453	
2) Nitrogen		1.2687			1.2687	
Acetic Acid			1.0000			
Ethyl Acetate				.0222	.0050	
Carbon Dioxide					.0209	
Carbon Monoxide					.0020	
Miscellaneous Organics						.0006
Total	.7905	1.6573	1.0000	.0222	1.3473	.0783

Total In = 2.4478 Total Out = 2.4478

TABLE ACE-II
ENERGY BALANCE
ACETIC ACID
VIA
ACETALDEHYDE OXIDATION
WITH
ACETALDEHYDE-ETHANOL FEED

There is insufficient data available on which to base an overall energy balance.

Heat of Reaction at 25° C (1)

$CH_3CHO\ (l) + \frac{1}{2}O_2\ (g) \xrightarrow{\qquad} CH_3COOH\ (l)$ H_R = 2337 BTU/Lb. Acetic Acid

$CH_3CH_2OH(l) + O_2\ (g) \xrightarrow{\qquad} CH_3COOH\ (l) + H_2O\ (l)$ H_R = 3651 BTU/Lb. Acetic Acid

$CH_3COOH\ (l) + C_2H_5OH\ (l) \xrightarrow{-H_2O} CH_3COOC_2H_5\ (l)$ H_R = 216 BTU/Lb. Acetic Acid

(2) Total heat evolved at 25° C by all reactions = 2635 BTU/Lb. Acetic Acid

(1) For liquid phase reaction.

(2) Using ethanol-acetaldehyde ratio from material balance - Table I

TABLE ACE-III
NATIONAL EMISSIONS INVENTORY
ACETIC ACID
VIA
ACETALDEHYDE OXIDATION

EPA Plant Code No.	2-5
Capacity - Tons of Acetic Acid/Yr.	182,500 (1)
Production - Tons of Acetic Acid/Yr	72,000
Emissions to Atmosphere	
Stream	Scrubber Vent
Flow - Lbs./Hr.	22,457
Flow Characteristic - Continuous or Intermittent	Continuous
if Intermittent - Hrs./Yr.	
Composition - Tons/Ton of Acetic Acid	
Acetaldehyde	.00481
Ethyl Acetate	.00502
Carbon Dioxide	.02089
Carbon Monoxide	.00202
Water	.00077
Oxygen	.04529
Nitrogen	1.26869
Analysis	Yes
Sample Tap Location	On-stream to control room
Frequency of Sampling	3 times/week
Type of Analysis	Gas Chromatograph - Orsat
Odor Problem	No
Vent Stacks	Yes
Number	1
Height - Ft.	75
Diameter - Inches	66
Exit Gas Temp. - F°	45
Flow - SCFM/Stack	5000
Emission Control Devices	Yes
Type	Two Absorbers
Summary of Air Pollutants	
Hydrocarbons - Ton/Ton Acetic Acid	.00983
Particulates - Ton/Ton Acetic Acid	0
NO_x - Ton/Ton Acetic Acid	0
SO_x - Ton/Ton Acetic Acid	0
CO - Ton/Ton Acetic Acid	.00202

(1) Published capacity.

TABLE ACE-1V
CATALOG OF EMISSION CONTROL DEVICES
ACETIC ACID
VIA
ACETALDEHYDE OXIDATION

ABSORBERS		
EPA Code No. for plant using	2-5 (1)	
Control Emission of	Acetic Acid, Ethyl Acetate, Ethanol, Acetaldehyde	
Absorbing Liquid	Water - 5% Acetic Acid (2)	
Type - Spray		
Packed Column		
Column w/trays	Yes	
Number of Trays	25	20
Tray Type	Bubble Cap	Bubble Cap
Absorbing Liquid Rate - GPM	80	80
Gas Rate - SCFM (lb./hr.)	5000	
T-T Height - Ft.	62	
Diameter - Ft.	78	
Washed Gases to Stack	Yes	
Stack Height - Ft.	75	
Stack Diameter - Inches	66	
Installed Cost - Mat'l. & Labor - $	230,000 (3)	
Installed Cost based on "year" - dollars	1970	
Installed Cost - ¢/lb. of Acetic Acid	.16	
Operating Cost - Annual - $ - 1972	45,130	
Value of Recovered Product - $/Yr.	198,000	
Net Operating Cost - Annual - $	(152,870)	
Net Operating Cost - ¢/lb. of Acetic Acid	(.106)	
Efficiency - % - SE - Acetic Acid	100	
Efficiency - % - SE - Ethanol	100	
Efficiency - % - SE - Ethyl Acetate	88.7	
Efficiency - % - SE - Acetaldehyde	97.8	
Efficiency - % - SERR	98.6	

(1) Two absorbers each with specification shown.
(2) Absorber is divided into two sections - the bottom section uses 5% acetic acid as the absorbing liquid and the top uses water
(3) Total cost for both absorbers.

TABLE ACE-V
NUMBER OF NEW PLANTS BY 1980
ACETIC ACID
VIA
ACETALDEHYDE

Current Capacity (1)	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity to be Added	Economic Plant Size	Number of New Plants
875	100	775	2,015 (2)	1240	400	3

(1) MM lbs./year.

(2) 45% of 4,500 MM lbs./year demand for acetic acid.

(3) Assumes 45% of new plants built will use acetaldehyde process, for further information, see Table HAC-V of this report.

TABLE ACE-VI
EMISSION SOURCE SUMMARY
ACETIC ACID
VIA
ACETALDEHYDE OXIDATION
T/T OF ACETIC ACID

Emission	Source	Total
	Absorber Vent	
Hydrocarbons	.00983	.00983
Particulates	0	0
NO_x	0	0
SO_x	0	0
CO	.00202	.00202

TABLE ACE-VII
WEIGHTED EMISSION RATES

Chemical Acetic Acid

Process Acetaldehyde Oxidation

Added Capacity 1240 MM Lbs./Year

Pollutant	Emissions Lb./Lb.	Increased Emissions MM Lbs./Year	Weighting Factor	Weighted Emissions MM Lbs./Year
Hydrocarbons	.00983	12.2	80	976
Particulates	0	0	60	0
NO_x	0	0	40	0
SO_x	0	0	20	0
CO	.00202	2.5	1	2.5

Significant Emission Index = 978.5

Acetic Anhydride

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I. Introduction

Acetic anhydride finds its largest applications in the production of cellulose acetate which can be spun into rayon and in the production of acetate resins and plastics. These uses account for 90 - 95% of the commercial acetic anhydride produced in this country. It is also used for drying explosives.*

Three main processes are used to make acetic anhydride. The predominant processes are the pyrolysis of acetic acid or acetone to form acetic anhydride via the ketene route. Oxidation of acetaldehyde to acetic acid and acetic anhydride, the so called dual process, is less widely used. Some acetic anhydride is also made starting with acetylene and acetic acid but the two ketene processes and the acetaldehyde dual process are the three main manufacturing routes.

Pyrolysis of acetic acid to acetic anhydride, the subject of this report, is the largest in terms of installed capacity.

There does not appear to be much in the way of air pollution from this process. Tail gas from the cracking and absorption sections can readily be flared to CO_2 and water. Some waste liquids are produced but these can either be biologically degraded or incinerated cleanly.

Current install capacity for acetic anhydride is 2,200 million lbs./year and about 1,500 to 1,600 MM lbs. represents produce made from pyrolysis of acetic acid. An additional 250 - 300 MM lbs. of capacity are projected between now and 1980.

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*In a 500 MM lb./year plant owned by the U. S. Army Munitions Command and operated for them by Eastman Kodak.

II. Process Description

Glacial acetic acid is vaporized and superheated to 1100° F under 200 mm absolute pressure. Catalyst such as triethyl phosphate is added to the system and the acetic acid vapors are fed to a cracking furnace at 1300° F where they pyrolize to ketene and water (90% per pass conversion) plus minor amounts of hydrocarbons, CO_2, CO and H_2. Cracked gases emerging from the furnace are quickly condensed and cooled to 32° F to remove weak unreacted acetic acid (35%) and to prevent reaction of the ketene formed with the weak acid.

Uncondensed concentrated ketene gas plus small quantities of hydrocarbons, CO, CO_2 and H_2 are directed to the second stage of the process where they are absorbed and scrubbed by concentrated acetic acid to form acetic anhydride in stages from 100° F down to 32° F. The basic reactions for the process are:

1. Pyrolysis of Acetic Acid

$$\underset{\text{60 m.w.}}{CH_3\,COOH} \xrightarrow[\text{Reduced Pressure}\ 1300^{\circ}\ F]{.\ \text{Cat}} \underset{\substack{\text{Ketene}\\ \text{42 m.w.}}}{CH_2{=}C{=}O} + \underset{\text{18 m.w.}}{H_2O}$$

Side Reactions

$$CH_3\,COOH \longrightarrow CH_4 + CO_2$$
$$CH_3\,COOH \longrightarrow 2\,CO + 2\,H_2$$
$$2\,CH_2{=}C{=}O \longrightarrow CH_4 + C^{o} + 2\,CO$$
$$2\,CH_2{=}C{=}O \longrightarrow CH_2 = CH_2 + 2\,CO$$

2. Reaction of Ketene with Acetic Acid

$$\underset{\substack{\text{Ketene}\\ \text{42 m.w.}}}{CH_2 = C{=}O} + \underset{\substack{\text{Acetic Acid}\\ \text{60 m. w.}}}{CH_3\,COOH} \xrightarrow{30^{\circ} - 100^{\circ}\ F} \underset{\substack{\text{Acetic Anhydride}\\ \text{102 m.w.}}}{CH_3\,CO{-}O{-}CO\,CH_3}$$

Tail gas from the absorption/scrubbing towers can be incinerated to CO_2 and water but one respondent vents this gas directly to the air. Acetic anhydride is concentrated and purified by distillation. Bottoms from this process consists of small quantities of "tar" which is normally burned.* Weak acetic acid is concentrated in a still and recycled back to the process as feed stock or absorbant. Water produced in the process and removed from the acetic acid is treated in plant before discharge to sewage. So called low boiling liquids removed from the acetic acid are usually incinerated. This is another very small stream.

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*It may also be land-filled.

III. Plant Emissions

A. Continuous Air Emissions

1. Tail Gas Vent

Tail gas from this process consists chiefly of hydrocarbons, CO_2, CO, H_2 and some air. One respondent burns this stream in a flare to CO_2, H_2O and some CO. Unfortunately, no composition of the flared gas is available but the concentration of CO should be very low, if not nil, in a well designed flare. The other respondent removes this gas from the process with steam jets and vents the jet exhaust to the atmosphere. If would not take much of a change to be able to flare this stream and cut plant emissions to virtually nothing except PPM of NO_x from air to the flare.

B. Intermittent Air Emissions

Furnace regeneration for eight hours every 60-90 days is the only reported emission of this type. Some CO and particulates are emitted along with CO_2.

C. Continuous Liquid Wastes

1. Waste Water

One respondent reports about 50 GPM of waste water from anhydride and acetic acid recovery containing about 2,400 lbs./day BOD. This waste water is treated. In addition, some 1,000 gal./min. of steam jet condensate and water scrubber effluent containing 300 lbs./day BOD are discharged without treatment.

The other respondent reports nothing on this subject but since water is an integral part of this process, he too must have a waste stream to get rid of somehow.

2. Waste Liquids Other Than Water

One respondent generates about 0.001 lbs. waste liquid/lb. acetic anhydride, which he incinerates. The other respondent reports nothing here but, again, the process does generate some waste liquids, which must be disposed of.

D. Solid Wastes

Tars from the acid and anhydride steps plus some catalyst are produced at a rate of about 0.0005 lbs./lb. of anhydride. These tars are either incinerated to CO_2, CO and H_2O (no composition available) or biologically treated and settled before discharge. Volatile components can be recovered from the tars, producing a coke-like material that is suitable for land-fill.

E. Odors

Neither respondent reported any odors. One might expect a typical pungent "acetic" odor on the plant site, but because of the 5 PPM TLV of acetic anhydride, process control seems to have prevented an odor problem.

F. Fugitive Emissions

None reported.

G. Other Emissions

Other than the possibility of SO_x and NO_x in the furnace flue gas, there are no other emissions associated with this process. One respondent reported burning natural gas, containing less than 10 PPM sulfur.

IV. Emission Control

The pyrolysis of acetic acid to acetic anhydride via ketene theoretically produces no by-products other than water. Practically, however, small amounts of hydrocarbons, CO, CO_2 and H_2 are produced as well as some low boiling liquids of composition approximating $(CH_x)_y$ CO or $(CH_x)_y$ CO_z H. The liquids are incinerated, presumably to CO_2 and H_2O although no flue gas analyses are available. The process tail gases are flared in one case and vented by another respondent. Gas from the flare is reported as CO_2, H_2O and CO although the latter should be virtually nil in a well designed flare.

Such data as are available are summarized in Table IV. The incinerator will have an efficiency (CCR & SERR)* approaching 100% if it is designed properly. There should be no noxious substances in the flue gas but there are no analyses to confirm this. No quantitative information is given on the performance of the flare used on the tail gas by one of the two respondents.

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*For a definition of these terms, see Appendix V.

V. Significance of Pollution

It is recommended that no in-depth study of this process be undertaken. Emissions from this process are inherently very low and a simple flaring can take care of all vented gases converting them to CO_2 and water.

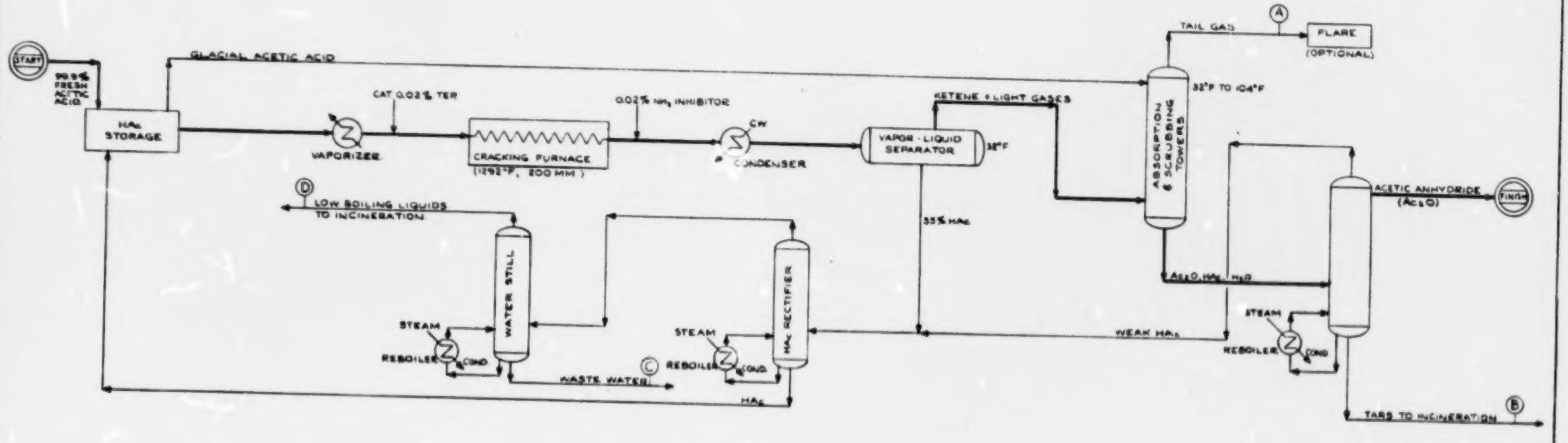
The Significant Emission Index* was estimated assuming all new installations will burn the tail gas in a flare and the one comparatively large venting of tail gas reported will not be flared (about 61% of the 1980 capacity). This is calculated to be 60, but if the one respondent flared his vent stream, not an unreasonable assumption as it should not be difficult, the SEI would drop to near zero. Further work on this process should be directed toward flaring this tail gas stream or recovering some of its heating value in the cracking furnace as supplemental fuel.

*For a definition of these terms, see Appendix IV of this report.

VI. Producers of Acetic Anhydride

Company	Location	Capacity, MM lbs./yr.
Celanese Corporation Celanese Chemicals & Celanese Fibres Company Divisions	Pampa, Texas Cumberland, Maryland Narrows, Va. Rock Hill, S. C.	850
	Rome, Ga.	N.A.
Eastman Kodak, Eastman Chemical Products, Inc.	Kingsport, Tenn.	550
FMC Corporation	Meadville, Pa.	60
Hercules, Polymers Dept.	Parlin, N. J.	20
Union Carbide, Chemicals & Plastics Division	Brownsville, Texas Texas City, Texas	225
U. S. Army Munitions Command (operated by Eastman Kodak)	Kingsport, Tenn.	500
		Total - 2,205

At least two-thirds of the above capacity represents the pyrolysis of acetic acid via ketene route to acetic anhydride.


START
99.9% FRESH ACETIC ACID
HAc STORAGE
GLACIAL ACETIC ACID
VAPORIZER
CAT 0.02% TEP
CRACKING FURNACE (1292°F, 200 MM)
0.02% NH_3 INHIBITOR
CW
CONDENSER
VAPOR - LIQUID SEPARATOR
32°F
KETENE + LIGHT GASES
35% HAc
TAIL GAS
Ⓐ
FLARE (OPTIONAL)
ABSORPTION & SCRUBBING TOWERS
32°F TO 104°F
Ac_2O, HAc, H_2O
ACETIC ANHYDRIDE (Ac_2O)
FINISH
WEAK HAc
STEAM
REBOILER
COND.
TARS TO INCINERATION
Ⓑ
Ⓓ
LOW BOILING LIQUIDS TO INCINERATION
WATER STILL
STEAM
REBOILER
COND.
WASTE WATER
Ⓒ
HAc RECTIFIER
STEAM
REBOILER
COND.
HAc

FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT No 68-02-0255

PREPARED BY
CATALYTIC, INC.
ENGINEERING DEPARTMENT, PHILADELPHIA, PENNA. 19102

FIG ANA-1
SIMPLIFIED FLOW DIAGRAM
ACETIC ANHYDRIDE FROM
ACETIC ACID VIA KETENE

SCALE	NONE	DATE
DRAWN BY	TTMA	4-18-73
CHECKED BY		
CATALYTIC APPROVAL		
CLIENT APPROVAL		

JOB NO 42030
424
DWG NO R-227
REV A

TABLE ANA-I
ACETIC ANHYDRIDE FROM ACETIC ACID

OVERALL MATERIAL BALANCE - TON/TON ACETIC ANHYDRIDE

MATERIAL IN	
Pure Acetic Acid	1.2000
Misc. Carboxylic Acids and Water	0.0011
	1.2011

MATERIAL OUT	
Acetic Anhydride	1.0000
Low Boiling Liquids	0.0010
Tars	0.0005
Water	0.1760
Flare Gas*	0.0206
Acetic Acid	0.0030
	1.2011

*H_2, Hydrocarbons, N_2, O_2, CO_2 CO

TABLE ANA-II
ACETIC ANHYDRIDE FROM ACETIC ACID
HEAT BALANCE

There is not enough data to calculate a detailed heat balance for this process. An estimate of the heat flows around the preheater, vaporizers and cracking furnace is:

HEAT IN	BTU/LB. ACETIC ANHYDRIDE
Sum of steam, heat exchange and fired heaters	2240
HEAT OUT	
Endothermic heat of reaction	1158
Differential enthalpy (Reaction products - feed)	1082
	2240

TABLE ANA-III
NATIONAL EMISSIONS INVENTORY
ACETIC ANHYDRIDE FROM ACETIC ACID (KETENE ROUTE)

Plant - EPA Code No.		3-2		3-1
Capacity, Tons Acetic Anhydride/Yr.	30,000 Est.	30,000 Est.	30,000 Est.	425,000
Range in Production, % of Max.	None Given	None Given	None Given	None Given
Emissions to Atmosphere	Final Scrubber Off-Gas	Tar Incinerator Flue Gas	Vaporizer Emergency Rupture Disc	Final Scrubber Off-Gas
Stream	Stream goes to flare no comp. of flared gas given			
Flow, Lb./Hr.	180	1458 Est.	Unknown	1800
Flow Characteristic, Continuous or Intermittent	Continuous	Continuous	Open only in emergencies	Continuous
Composition, Lb./Lb. Acetic Anhydride				
Particulate	+	+		
Carbon Dioxide	0.00405	+		0.002907
Carbon Monoxide	0.00975	+		0.008144
Propodiene	0.00112			0.000021
Ethylene	0.00368			0.003113
Methane	0.00279			0.002660
Water	0.00241	+	0.2%	
Ethane	0.00010			0.000082
Diketene	0.00007			
Acetic Anhydride	0.00050			
Oxygen	0.00034			0.000433
Nitrogen	0.00136			0.001856
Acetic Acid			99.8%	0.0000007
Hydrogen				0.000144
Propane				0.001258
Vent Stacks	No Data		None	
Number				2
Height, Ft.				90 75
Diameter, Inches				8 6
Exit Gas Temp. °F		1400° F		100
SCFM/Stack		Unknown	Normally Closed	300 60
Emission Control Devices				
Flare/Incinerator	Incinerator	Incinerator	None	None
Absorber/Scrubber				
Analysis				
Date or Frequency of Sampling	Never	Never	Never	Annually
Sample Tap Location		Stack Top		Sump
Type of Analysis	Calculated	None		G.C.
Odor Problem	No	No		No
Summary of Air Pollutants	No Data	No Data	Not App	
Hydrocarbons - Lb./Lb. Acetic Anhydride				0.004474
Aerosols & Particulates - Lb./Lb. Acetic Anhydride				0
NO_x - Lb./Lb. Acetic Anhydride				0
SO_x - Lb./Lb. Acetic Anhydride				0
CO - Lb./Lb. Acetic Anhydride				0.008144

TABLE ANA-IV
CATALOG OF EMISSION CONTROL DEVICES

INCINERATION DEVICES			
EPA Code No. for plant using	3-2	3-2	3-1
Flow Diagram (Fig. I) Stream	A	B	C
Device No.	F-101	I-101	I-102
Type of Compound Incinerated	Hydrocarbons	Organic Tars	Organics, Hydrocarbons
Type of Device	Flare	Incinerator	Incinerator
Material Incinerated SCFM (lb./hr.)	40	1458	(83)
Auxilliary Fuel Req'd.			
Type			
Rate BTU/Hr.			
Device or Stack Height, Ft.	Not Given	Not Given	Not Given
Installed Cost - Mat'l. & Labor - $	" "	" "	" "
Installed Cost based on "year" - dollars	" "	" "	" "
Installed Cost, ¢/lb. of Acetic Anhydride - Year	" "	" "	" "
Operating Cost - Annual - $	" "	" "	" "
Operating Cost - ¢/lb. of Acetic Anhydride	" "	" "	" "
Efficiency - % - CCR	?	?	?
Efficiency - % - SERR	?	?	?

TABLE ANA-V
NUMBER OF NEW PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity* to be Added	Economic Plant Size	Number of New Units
1705**	0	1705	2050	2100	267	100	2 - 3

NOTE: All capacities in millions of lbs./year.

*Capacity using pyrolysis of HAC route only.

**Excludes U. S. Army Munitions Report

TABLE ANA-VI
EMISSION SOURCE SUMMARY
TON/TON ACETIC ANHYDRIDE

Emission	Source			Total
	Absorber-Scrubber Tail Gas	Tar Incinerator Gas	Fugitive Emissions	
Hydrocarbons	0.002729	0	None Given	0.002729
Particulates & Aerosols	0	TR		TR
NO_x	0	0		0
SO_x	0	0		0
CO	0.004968	+		0.004968

NOTE: (+) Compound present but no analysis available.

TABLE ANA-VII
WEIGHTED EMISSION RATES

Chemical Acetic Anhydride

Process Pyrolysis of Acetic Acid

Increased Capacity by 1980 267 MM lbs., assume 1133 MM lbs. in 1973

Pollutant	Emissions lb./lb.	Emissions MM lb./yr.	Weighting Factor	Weighted Emissions MM lb./yr.
Hydrocarbons	0.002729	0.73	80	58.4
Aerosols	TR	TR	60	0
NO_x	0	0	40	0
SO_x	0	0	20	0
CO	0.004968	1.42	1	1.42

Significant Emission Index = 59.87

Adipic Acid

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I. Introduction

Ninety percent of all adipic acid produced is used in the manufacture of nylon 6,6. Adipic acid is condensed with hexamethylene-diamine to form nylon salt; this requires 0.7 lbs. of adipic acid/lb. of nylon 6,6. Additionally some hexamethylene-diamine is derived from adipic acid; this requires 1.05 lbs. of adipic acid/lb. of nylon 6,6. Thus, the current demand and the future growth of adipic acid is closely bound to the nylon 6,6 market. Of lesser importance is adipic acid's use in the production of plasticizers, synthetic lubricants and urethanes.

Practically all commercial production of adipic acid is based on oxidizing cyclohexanone/cyclohexanol with nitric acid. The various oxides of nitrogen produced during the oxidation constitute the principal source of air pollution for this process. The separation of adipic acid from its various by-products-primarily glutaric and succinic acid - and the purification of adipic acid contribute only slightly to the overall air pollution. Likewise; the pneumatic conveying, drying and melting of the purified adipic acid crystals contribute relatively little to the total air emissions produced by the process as a whole. Air pollution resulting from the production of adipic acid can be characterized as being moderate.

The current U. S. capacity for the production of adipic acid is 1.43×10^9 lbs./yr. 1980 production capacity, based on an annual growth rate of 5.5%(1), is estimated at 2.20×10^9 lbs./yr.

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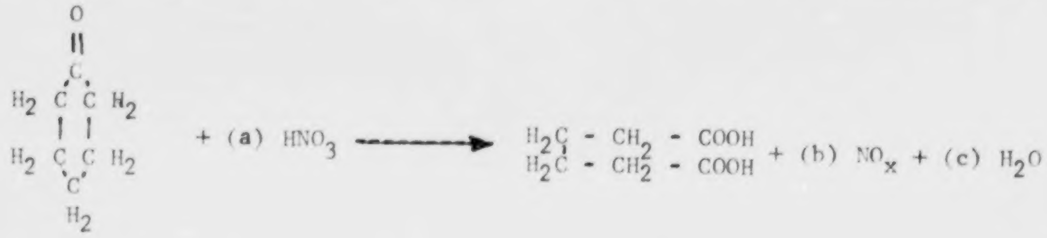
(1) Chemical Marketing Reporter, April 24, 1972

II. Process Description

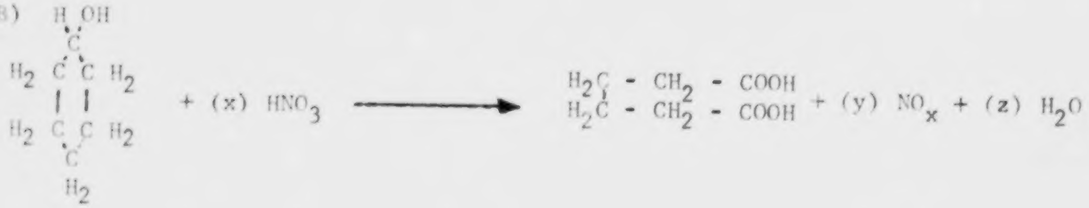
Cyclohexanone and cyclohexanol are oxidized to adipic acid by reaction with nitric acid. The following two equations illustrate the gross chemistry:

(A)



Cyclohexanone + Nitric Acid ⟶ Adipic Acid + Nitrogen Oxide + Water

(B)



Cyclohexanol + Nitric Acid ⟶ Adipic Acid + Nitrogen Oxide + Water

The nitrogen compounds formed, shown above as NO_x, are predominately NO, NO_2 and N_2O. Additionally, various organic acid by-products are produced, chief among these are acetic acid, glutaric acid and succinic acid; in larger plants some of these may be recovered and sold.

The following process description may more easily be followed by referring to Figure I - a process flow diagram:

In commercial practice a mixture of cyclohexanone/cyclohexanol is oxidized in a series (generally two) of stirred tank reactors. Feed to the reactors is approximately one part alcohol-ketone and **five** parts 50 wt. % nitric acid. Pressure is about 30 psig and temperature is maintained at 170° to 180° F by water cooling or heat exchange. Standard catalyst for the oxidation is a mixture of cupric nitrate and ammonium vanadate.

Subsequent to the oxidation the dissolved NO_x gases plus any light hydrocarbon by-products are stripped from the adipic acid/nitric acid solution with air and steam. NO and NO_2 are recovered by absorption in nitric acid.

The stripped adipic acid/nitric acid solution is then chilled and sent to the No. 1 crystallizer, where crystals of adipic acid are formed. The crystals are separated from the mother liquor in the No. 1 centrifuge and transported to the adipic acid drying and/or melting facilities. The mother liquor is separated from the remaining uncrystallized adipic acid in the product still and recycled to the reactors.

The bottoms from the product still are diluted with water, rechilled and pumped to the No. 2 crystallizer. The slurry from the No. 2 crystallizer is pumped to the No. 2 centrifuge where the remaining adipic acid crystals are separated from the diluted residual mother liquor. The crystals are combined with the product from the No. 1 centrifuge. The mother liquor is distilled to recover the nitric acid; the residual material is sent to waste disposal.

III. Plant Emissions

A. Continuous Air Emissions

1. Reactor Off-gas

All adipic acid plants that oxidize cyclohexanone/cyclohexanol mixtures with nitric acid produce NO_x. Much of the NO_x formed is recovered as nitric acid, but a significant portion is emitted to the atmosphere. The NO_x emissions reported varied from .03 to .34 lbs. of NO_x per lb. of adipic acid produced. This tenfold variation in emission rates is apparently the result of two factors; (1) the difference in the performance of NO_x recovery systems and (2) the variation in the percentage of N_2O in the NO_x - this is a factor because N_2O cannot be easily recovered as nitric acid. (N_2O/NO_x ratio is dependent to some extent on cyclohexanol/cyclohexanone ratio). Reactor off-gas emissions are summarized in Table III. Note, however, that N_2O is not considered a pollutant.

2. Adipic Acid Purification and Nitric Acid Recovery Vents

Because of the variation in processing schemes and the interrelationship of the two above named operations it is difficult to make generalized distinctions between the subject streams. Air emissions from these two sources share a similarity in composition - they are predominantly NO_x. In most instances, nitric acid recovery operations succeed in minimizing emissions. One operator (EPA Code 5-2); however, does report venting significant amounts (.03 lb./lb.) of NO_x from these facilities. These emissions are summarized in Table III.

3. Vents from Adipic Acid Conveyors, Driers and Melters

The drying, conveying and general handling of adipic acid crystals presents the same problems that most dry solids present. The 'handling' produces 'fines' and the fines generate dust. The respondents report utilizing [illegible] variety of dust control equipment; cyclones, bag filters and wet scrubbers. In general, the particulate emissions from this source are low. The highest rate of particulate emissions reported - by EPA Code No. 5-4 - was .0005 lbs./lb. of adipic acid. Table III contains a complete summary of all reported emissions in this category.

4. Plant Flare and Incinerator Flue Gases

Most petrochemical plants employ flares, 'thermal oxidizers' or some type of incineration devices to burn waste hydrocarbons; either on a continuous basis, or intermittently, during plant emergencies. Adipic acid plant operators are no different, in this respect, than operators of other types of petrochemical plants. They have reported the use of various incineration devices; however, in order to "burn" NO_x containing gases in such a way that the 'combustion' products are less offensive than their 'uncombusted' precursors, the incineration devices must be specially designed to decompose NO_x into N_2 and O_2. At least one respondent has indicated that such a special incinerator is indeed utilized (EPA Code No. 5-3, Device AA-8). Flue gases from less specialized devices must be suspected of containing practically all of the NO_x that was fed to them. This information is summarized in Table IV.

5. Storage Losses

No respondent has offered an estimate of storage losses. They should be quite low for two reasons, (1) final product is a solid and not subject to evaporation and (2) the hydrocarbon feed frequently comes direct from a previous processing step, and hence is not subject to normal storage losses. Both operators EPA Code 5-2 and 5-4 report using absorbers/scrubbers on nitric acid storage tank vents, thus minimizing emissions from that source. Therefore, although no quantitative data are avaliable it seems safe to surmise that air emission from adipic acid plant storage facilities are low.

B. Intermittent Air Emissions

Start-up and Emergency Vents

This type of emission is universally encountered in the pertochemical industry and will vary from process-to-process, from operator-to-operator and even from year-to-year. One operator (EPA Code No. 5-2) estimates that he vents his reactors to the atmosphere - on an emergency basis - six to twelve times per year. Taking the higher figure this still amounts to less than one ton per year of NO_x - an insignificant amount. This information is detailed in Table III.

C. Continuous Liquid Wastes

Waste Water

All respondents report the production of waste water:

Operator EPA Code 5-1 reports 90 GPM, which is disposed of by deep well injection.

Operator EPA Code 5-2 reports 600 GPM, containing 0.5 wt. % succinic acid and 1.2 wt. % glutaric acid. Its method of disposal is not discussed.

Operator EPA Code 5-3 reports the production of about 350 GPM, containing 0.9 wt. % HNO_3 and 2.3 wt. % organics. Deep well injection is used for disposal.

Operator EPA Code 5-4 reports the production of about 40 GPM of waste water.

D. Intermittent Liquid Wastes

No intermittent liquid wastes were reported.

E. Solid Wastes

No solid wastes were reported.

F. Fugitive Emissions

Only one operator (EPA Code No. 5-1) has made a quantitative estimate of fugitive emissions. His estimate is 150 SCFH (of NO_x?).

Other operators state that emissions of this type are either nonexistent or very low. Considering that the adipic acid process is low pressure, and that fugitive emissions would probably be fairly easy to detect because of their odor or their visibility, it is probable that fugitive emissions are quite low.

G. Odors

In general, the production of adipic acid via nitric acid oxidation of cyclohexanol/cyclohexanone does not appear to be a process that has an odor problem.

None of the respondents reported an odor complaint in the past year. Most of the reported odors are said to be detected only on the plant property and only at intermittent intervals. The odiferous materials are usually identified as NO_x.

All NO_x containing vent streams are potential sources of odors. However, according to the questionnaire these streams are well enough controlled to prevent odor problems.

IV. Emission Control

The emission control devices that have been reported as being employed by operators of adipic acid plants are summarily described in Table IV of this report. An efficiency has been assigned each device whenever data sufficient to calculate it have been available. Three types of efficiencies have been calculated:

(1) "CCR" = Completeness of Combustion Rating

$$CCR = \frac{\text{lbs. of } O_2 \text{ reacting (with pollutants in device feed)}}{\text{lbs. of } O_2 \text{ that theoretically could react}} \times 100$$

(2) "SE" - Specific Efficiency

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

(3) "SERR" - Significance of Emission Reduction Rating

$$SERR = \frac{(\text{pollutant} \times \text{weighting factor}^*) \text{ in} - (\text{pollutant} \times \text{weighting factor}^*) \text{ out}}{(\text{pollutant} \times \text{weighting factor}^*) \text{ in}} \times 100$$

*Weighting factor same as Table VII weighting factor.

Normally a combustion type control device (i.e., incinerator, flare, etc.) will be assigned both a "CCR" and a "SERR" rating, whereas, a non-combustion type device will be assigned an "SE" and/or an "SERR" rating. A more complete description of this rating method may be found in Appendix V of this report.

Although efficiency ratings for most devices are shown in Table IV, a few general comments regarding adipic acid pollution control device performance seems in order:

Absorbers

Adipic acid plant operators reported the use of five absorbers. They are identified in Table IV as devices AA-1, AA-2, AA-3, AA-4, and AA-7. The specific efficiencies (with regard to NO_x, but excluding N_2O since it is not regarded as a pollutant) range from 48% to 98.8%. Information sufficient to determine the cause of device AA-7's unusually low efficiency (i.e., 48%) is not available. Three of the other four devices have specific efficiencies greater than 95%, while insufficient data precluded the calculation of an efficiency for the third. Thus, based on the data reported in the questionnaires, absorbers in adipic acid 'NO_x service' appear capable of removing 95 + % of NO and NO_2.

Scrubbers

The operator of plant EPA Code No. 5-2, reports the use of two scrubbing devices, AA-5 and AA-6, to control the emission of adipic acid dust. His estimates of adipic acid concentrations lead to calculated specific efficiencies of about 90% for both devices. This is probably typical for this service, but variations in particle size distribution and device energy input will alter efficiency.

Cyclones

The use of two cyclone separators has been reported by questionnaire respondents. Particle size information is lacking for both installations. Based on the scant information available on these devices it seems safe to say only that adipic acid dust collection efficiencies in excess of 90% are feasible with single stage cyclones.

Bag Filters

The operator of plant EPA Code No. 5-3 provides the only information on the use of bag filters in the control of adipic acid dust emissions. Although he does not report particle size, he states dust collection efficiency is 100%.

Incineration Devices

Pollution reduction via the incineration of nitrogen oxides requires the use of devices specifically designed for this duty. These special burners reduce NO_x to elemental nitrogen by providing a reducing atmosphere through the use of at least 10% excess fuel. NO_x reductions of 75 to 90% have been reported for this method in the literature. The operator of plant EPA Code No. 5-3 reports utilizing such a device for "burning" the NO_x fumes vented from his nitric acid storage facilities. Data provided by that respondent show that his NO_x burner, identified as device AA-8 in Table IV, operates with an efficiency (CCR & SERR) of 70%. However, the same respondent reports sending another NO_x bearing stream - the effluent from device AA-7 - to the boiler house, where he states "an indeterminate amount of NO and NO_2 are reduced to N_2 in the burner flame". It seems extremely unlikely that the proper conditions for NO_x reduction exist within a boiler firebox.

Operator EPA Code No. 5-4 reports burning about 25 gallons an hour of various waste organic acids. His analysis of incinerator flue gases show his device to be 100% efficient in this duty.

It is unlikely that any change in operating conditions, per se, will lead to a significant decrease in air pollution. However, many adipic acid plants would benefit through more extensive use of pollution control equipment currently in use by some segments of the industry. As previously pointed out, with few exceptions, most of the devices that are employed have efficiencies in excess of 90% and better utilization of them could reduce the industry wide pollution average significantly.

Developmental work directed toward reductions in emissions from this process falls into the following general categories:

(1) One-step oxidation of cyclohexane to adipic acid - thereby reducing the number of pollution generating steps in the overall process by 50%.

(2) Substitution of air or preferably oxygen for nitric acid - as the oxidant. Although this has been studied and found uneconomic, further investigation of the overall environmental impact might be warranted.

(3) Devise method for economically recovering N_2O. Although not a

pollutant, N_2O recovery might lead to an overall reduction in nitric acid production if it could be re-oxidized and recycled.

(4) More efficient design and operation of devices currently being utilized.

V. Significance of Pollution

It is recommended that no in-depth study of this process be undertaken at this time. The reported emission data indicated that the quantity of pollutants released as air emissions is less for the subject process than for other processes that are currently being surveyed. However, one must be cognizant of the fact that although the production of adipic acid a the production of cyclohexanol/cyclohexanone were surveyed as two separate and individual processes, current practice is to integrate the production facilities into one plant. Therefore, the emissions accompanying 'one process' co-exist with the emissions from the other. This may give rise to consideration of an in-depth study of the entire process (cyclohexane to adipic acid) at some later date.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980 and to estimate the total weighted annual emissions from these new plants. This work is summarized in Tables V, VI and VII.

The Table V forecast of new plants is based on a predicted annual capacity growth of 5.5%. This is in agreement with the estimate published in the Chemical Marketing Reporter, April 24th, 1972.

On a weighted emission basis a Significant Emission Index of 780 has been calculated in Table VII. This is less than the SEI's for some of the other processes in the study. Hence, the recommendation to exclude adipic acid production from the in-depth study portion of the overall scope of work. However, due to the fact that most of the SEI results from NO_x emissions, any effort to reduce this type of pollution should certainly consider new source standards on adipic acid production.

VI. Adipic Acid Producers

The following tabulation of producers of adipic acid indicates published production capacity by company and location:

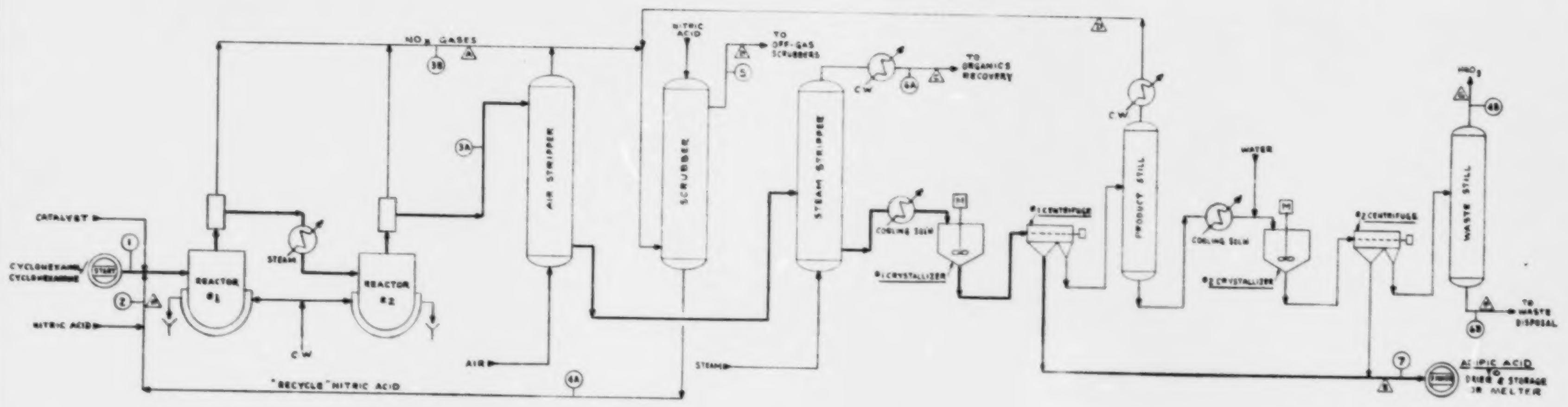
Company	Location		Capacity [(1)]
Allied	Hopewell, Va. (2)		20
Celanese	Bay City, Texas (3)		130
DuPont	Orange, Texas (3)		300
	Victoria, Texas (3)		300
El Paso	Odessa, Texas (3)		80
Monsanto	Luling, La. (2)		60
	Pensacola, Fla. (3)		540
		Total	1,430

Notes

(1) Capacity in MM Lb./Yr.

(2) Cyclohexanone/cyclohexanol derived from phenol.

(3) Cyclohexanone/cyclohexanol derived from cyclohexane.


CATALYST
CYCLOHEXANE/CYCLOHEXANONE
START
NITRIC ACID
1
2
REACTOR #1
STEAM
REACTOR #2
C W
NO_x GASES
3B
3A
AIR STRIPPER
AIR
"RECYCLE" NITRIC ACID
4A
NITRIC ACID
SCRUBBER
5
TO OFF-GAS SCRUBBERS
STEAM STRIPPER
STEAM
C W
6A
TO ORGANICS RECOVERY
COOLING SOL'N
#1 CRYSTALLIZER
#1 CENTRIFUGE
PRODUCT STILL
C W
WATER
COOLING SOL'N
#2 CRYSTALLIZER
#2 CENTRIFUGE
WASTE STILL
HNO3
6B
TO WASTE DISPOSAL
7
STORE
ADIPIC ACID TO DRIER & STORAGE OR MELTER

NOTES

1- ▲ = LOCATION OF POLLUTION CONTROL DEVICE – SEE TABLE IX

2 ⓝ = MATERIAL BALANCE STREAM - SEE TABLE I

3 THERE ARE MANY VARIATIONS OF THIS PROCESS, SOME OF WHICH MAY BE SIGNIFICANTLY DIFFERENT THAN THE PRESENTED SCHEME

[illegible]	NONE	[illegible]
[illegible]	E C A	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]		

FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO. 68-0[illegible]

PREPARED BY
CATALYTIC, INC.
[illegible]

FIGURE [illegible]
ADIPIC ACID PRODUCTION
VIA NITRIC ACID OXIDATION
OF CYCLOHEXANONE/CYCLOHEXANOL

PROJECT 42010
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R-210
A

TABLE AA-I
TYPICAL ADIPIC ACID PLANT
MATERIAL BALANCE
T/T OF ADIPIC ACID

Stream No. (Fig. I)	1	2	3 (A & B)	4 (A & B)	5	6 (A & B)	7
	Organic Feed to Oxidizer	Acid Feed to Oxidizer	Oxidizer Effluent	Nitric Acid to Recycle & Concen.	Light Ends	Heavy Ends	Adipic Acid
Cyclohexanone	.3402						
Cyclohexanol	.2778						
Cyclohexyl Esters (as formate)	.1399						
Adipic Acid			1.0000				1.0000
Dicarboxylic Acids (as succinic)			.0624			.0624	
Monocarboxylic Acids (as acetic)			.0357			.0357	
Water		1.8434	2.0130	2.0130			
Nitric Acid (100%)		2.0813	1.2193	1.2193			
Nitrogen Oxides (NO_2, NO, N_2O)			.3522		.3522		
Total	.7579	3.9247	4.6826	3.2323	.3522	.0981	1 0000

TABLE AA-II
ADIPIC ACID PRODUCTION
VIA
NITRIC ACID OXIDATION
OF
CYCLOHEXANONE/CYCLOHEXANOL

GROSS REACTOR HEAT BALANCE

Heat In	BTU/LB. OF ADIPIC ACID PRODUCED
Exothermic Heat of Reaction	1390*
Heat Out	
Reactor Temp. Control (@ 180° F)	1030
NO_x Vapor Vent	20
Sensible Heat Removal - Heat Exchange	170
Sensible Heat Removal - Cooling (to 60° F)	170
Total	1390

*Based on feed, conversions, etc. shown in Table 5.

TABLE AA-III
NATIONAL EMISSIONS INVENTORY
ADIPIC ACID PRODUCTION
VIA
NITRIC ACID OXIDATION OF CYCLOHEXANOL/CYCLOHEXANONE

Plant - EPA Code No.		5-1	
Capacity, Tons of Adipic Acid/Yr.		65,000	
Average Production, Tons of Adipic Acid/Yr.			
Range in Production - % of Max.		0	
Emissions to Atmosphere			
Stream	Reactor Vent		Combined HNO_3 Conc & Prod Purification Vent
Flow - lbs./hr.	7796		Unknown
Flow Characteristic, Continuous or Intermittent	Continuous		Continuous
if Intermittent, hrs./yr. flow			
Composition, Ton/ton of Adipic Acid			
Nitric Oxide	.00363		
Nitrogen Dioxide			00008
Nitrous Oxide	.33846		
Nitrogen	.06726		
Oxygen	.01539		
Carbon Monoxide			
Carbon Dioxide	.05286		
Water	.00215		
Adipic Acid			
Nitric Acid			
Vent Stacks	Yes		Yes
Number	1		1
Height - Ft.	140		63
Diameter - Inches	42		8
Exit Gas Temp. - F°	70		110
SCFM/Stack	1260		Unknown
Emission Control Devices	Yes - AA-1		Yes - AA-2
Absorber/Scrubber	+		+
Incinerator/Flare			
Condensor/K. O. Drum			
Other			
Analysis			
Date or Frequency of Sampling	Varies		Never
Tap Location			None
Type of Analysis	Phenoldisulfonic Acid		Estimate
Odor Problem	No		No
Summary of Air Pollutants			
Hydrocarbons, Ton/Ton of Adipic Acid		0	
Particulates, Ton/Ton of Adipic Acid		0	
NO_x - Ton/Ton of Adipic Acid		.00371	
SO_x - Ton/Ton of Adipic Acid		0	
CO - Ton/Ton of Adipic Acid		0	

TABLE AA-III
NATIONAL EMISSIONS INVENTORY
ADIPIC ACID PRODUCTION
VIA
NITRIC ACID OXIDATION OF CYCLOHEXANOL/CYCLOHEXANONE

Page 2 of 4

Plant - EPA Code No.			5-2			
Capacity, Tons of Adipic Acid/Yr.			270,000			
Average Production, Tons of Adipic Acid/Yr.						
Range in Production - % of Max.			0			
Emissions to Atmosphere						
Stream	Reactor Emergency Vent	Reactor Off-Gas	Prod. Purification Vent	Adipic Acid Drier Vent	**Adipic Acid Melter** Vent	Nitric Acid Recovery Vent
Flow - lbs./Hr.	~12,500	5567	2903	80,963	2220	58,550
Flow Characteristic, Continuous or Intermittent	Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous
if Intermittent, Hrs./Yr. Flow	<0.1					
Composition, Ton/ton of Adipic Acid						
Nitric Oxide	<.00001	.00005	.00003			
Nitrogen Dioxide	<.00001	.00008	.00005			.0110
Nitrous Oxide	<.00001					.0169
Nitrogen	<.00001	).07564	).03954	)1.12003		.2971
Oxygen		)	)	)		.4521
Carbon Monoxide	<.00001					.0141
Carbon Dioxide	<.00001					
Water	<.00001					.0451
Adipic Acid		.00376	.00185	.03659	.03171	
Nitric Acid				.00014	<.00001	
					<.00001	
Vent Stacks	Yes	Yes	Yes	No	Yes	Yes
Number	2	2	3		2	1
Height - Ft.	100	80	90		85	75
Diameter - Inches	24	12	12		8	4
Exit Gas Temp. - F°	170	120	120		180	80
SCFM/Stack	1000	~625	~220		~390	
Emission Control Devices	No	Yes - AA-3	Yes - AA-4	Yes - AA-5	Yes - AA-6	No
Absorber/Scrubber		+	+	+	+	
Incinerator/Flare						
Condenser/H. O. Drum						
Other						
Analysis						
Date or Frequency of Sampling	Never	Never	Never	Never	Never	
Tap Location	None		None	None	None	Accessible
Type of Analysis	Calc.	Calc.	Calc.	Calc. or Est.	Calc.	Various
Odor Problem	No	No	No	No	No	No
Summary of Air Pollutants						
Hydrocarbons, Ton/Ton of Adipic Acid			0			
Particulates, Ton/Ton of Adipic Acid			.00014			
NO_x, Ton/Ton of Adipic Acid			.0300			
SO_x, Ton/Ton of Adipic Acid			0			
CO , Ton/Ton of Adipic Acid			0			

TABLE AA-III
NATIONAL EMISSIONS INVENTORY
ADIPIC ACID PRODUCTION
VIA
NITRIC ACID OXIDATION OF CYCLOHEXANOL/CYCLOHEXANONE

Page 3 of 4

Plant - EPA Code No.		5-3				5-4	
Capacity - Tons of Adipic Acid/Yr.		150,000				40,000	
Average Production, Tons of Adipic Acid/Yr						40,000	
Range in Production - % of Max.		0				0	
Emissions to Atmosphere							
Stream	Reactor (A) Vent	HNO3 Recovery Vent	Prod. Purif. Vent	Pneumatic Conveyor Vent	Process (B) Vent Header	Adipic Acid Drier Vent	Heavy Ends Incinerator Flue Gas
Flow - lbs./Hr.	30,000	5,000	26,000	13,500	5597	45,169	8866
Flow Characteristic, Continuous or Intermittent if Intermittent, Hrs./Yr. Flow	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous
Composition - Ton/Ton of Adipic Acid							
Nitric Oxide	)	)					
Nitrogen Dioxide	).0259	).00010					
Nitrous Oxide	.2464	)			.06834		
Nitrogen	.45155	)1.00334	).86957	).45155	.36274	)4.43000	.65516
Oxygen	.05218	)	)	)	.08299	)	.04047
Carbon Monoxide					.00046		
Carbon Dioxide	.14650				.04514		.11130
Water	.01204					.08640	.07968
Adipic Acid						.00050	
Nitric Acid			.00009				
Vent Stacks	No	Yes	Yes	Yes	No (C)	Yes	Yes
Number		1	1	1		1	1
Height - Ft.		64	64	64		33	34
Diameter - Inches		36	36	36		18	48
Exit Gas Temp. F°		1832°	150°	150°		160	1400
SCFM/Stack						10,200	2,000
Emission Control Device	Yes - AA-7	Yes AA-8	Yes - AA-9	Yes - AA-10	Yes (C)	Yes - AA-11	Yes - AA-12
Absorber/Scrubber	+			+			
Incinerator/Flare		+			+		+
Condenser/K. O. Drum							
Other	+ steam boiler		+ bag filter	+ cyclone sep.		+ cyclone sep	
Analysis							
Date or Frequency of Sampling	Infrequently	Never	Never	Never	Infrequent	Never	Never
Sample Tap Location		None	None			None	None
Type of Analysis	Mass Spec.	Calc.	Calc.	Estimate	GLC	Estimate	Calc
Odor Problem	No	No	No	No	No	No	No
Summary of Air Pollutants							
Hydrocarbons, Ton/Ton of Adipic Acid		0				0	
Particulates, Ton/Ton of Adipic Acid		.00009				.00050	
NO_x, Ton/Ton of Adipic Acid		.026				.003	
SO_x, Ton/Ton of Adipic Acid		0				0	
CO , Ton/Ton of Adipic Acid		0				.00046	
		0					

TABLE AA-III

Page 4 of 4

EXPLANATION OF NOTES
NATIONAL EMISSIONS INVENTORY

ADIPIC ACID PRODUCTION
VIA
NITRIC ACID OXIDATION OF CYCLOHEXANONE/CYCLOHEXANOL

A) Operator states that this stream is sent to boiler house and used as 'air' for burners, where upon an unknown amount of $NO_x \longrightarrow N_2 + O_2$. Composition reported in Table III (ton/ton) is based on assumption that NO_x is reduced by 20% by this treatment. Actual NO_x concentration may increase or (under special conditions) be reduced by up to 90%.

B) Operator states that this stream is sent to HMD plant 'thermal oxidizer'. It is assumed that this device is especially designed for NO_x reduction. Consequently, a NO_x reduction of 70% (which is reported performance of device AA-8) has been assumed and the NO_x concentration reported in this column is correspondingly decreased.

C) No vent stack for this stream in adipic acid plant. Stream sent to thermal oxidizer in HMD plant.

TABLE AA-IV

CATALOG OF EMISSION CONTROL DEVICES

ADIPIC ACID PRODUCTION VIA NITRIC ACID OXIDATION OF CYCLOHEXANOL/CYCLOHEXANONE   Page 1 of 4

	Reactor Vent			Adipic Acid Purification		Nitric Acid Recovery
ABSORBERS/SCRUBBERS		I			III	
EPA Code No. for plant using	5-1	5-2	5-3	5-1	5-2	
Flow Diagram (Fig. II) Stream I.D.	A	A.	A.	A C.D.E C	.A.A.A.	
Device I.D No.	AA-1	AA-3	AA-7	AA-2	AA-4	
Controls Emission of -	NO_x	NO_x	NO_x	NO_x	NO_x	
Scrubbing/Absorbing Liquid	Water	Alkaline Water	Not Specified	Caustic	Alkaline Water	
Type - Spray	Not Specified			Not Specified		
Packed Column		+				
Column w/trays					+	
Number of trays						
Kind of tray						
Plenum Chamber						
Other						
Scrubbing Absorbing Liquid Rate - GPM	4	60			30	
Design Temp. (Operating Temp.) F°	100	180			160	
Gas Rate, SCFM (lb./hr.)	1204	650		110	170	
T-T Height, Ft.		25			24	
Diameter, Ft.		2.5			1.5	
Washed Gases to Stack -	Yes	Yes	No	Yes	Yes	
Stack Height - Ft.	140	80		63	90	
Stack Diameter - Inches	42	12		8	12	
Installed Cost - Mat'l. & Labor - $	360,000	40,000	33,000	120,000	60,000	
Installed Cost Based on - "year" - dollars	1965-1970	1971	1948	1964	1971	
Installed Cost - ¢/lb. of Adipic Acid/Yr.	.2769	.0074	.0110	.0923	.0111	
Operating Cost - Annual (1972)	57,000	6,000		10 000	9,000	
Value of Recovered Product, $/yr.	74,000	0		0	0	
Net Operating Cost - Annual, $	- 17,000	6,000		10,000	9,000	
Net Operating Cost - ¢/lb. of Adipic Acid		.0011		.0077	.0017	
Efficiency - % SE	95.9% (NO_x)	98.5% (NO_x)	48% (NO_x)		98.8% (NO_x)	
INCINERATION DEVICES						
EPA Code No. for plant using				5-4		5-3
Flow Diagram (Fig. II) Stream I.D.				F		C. H.
Device I.D. No.				AA-12		AA-8
Type of Compound Incinerated				Organic Acid		NO_x
Type of Device - Flare						
Incinerator				+		+
Other						
Material Incinerated, SCFM (lb./hr.)				0.46 GPM		(50,000) Total
Auxilliary Fuel Req'd. (excl. pilot)						Yes
Type						Nat. Gas
Rate - BTU/hr.						
Device or Stack Height - Ft.				34		64
Installed Cost - Mat'l. & Labor - $						100,000
Installed Cost Based on "year" dollars						1960-1965
Installed Cost - ¢/lb. of Adipic Acid/Yr.						.0333
Operating Cost - Annual - $ (1972)						14,600
Operating Cost - ¢/lb. of Adipic Acid						.0049
Efficiency - CCP - %				100		70
Efficiency - SEPR - %				100		70

TABLE AA-IV
CATALOG OF EMISSION CONTROL DEVICES
ADIPIC ACID PRODUCTION VIA NITRIC ACID OXIDATION OF CYCLOHEXANOL/CYCLOHEXANONE

Page 2 of 4

"Finished' Product Operations
Conveying, Drying, Melting, etc.

ABSORBERS/SCRUBBERS	1	1
EPA Code No. for plant using	5-2	5-2
Flow Diagram (Fig. II) Stream I.D.	.f.	.f.
Device I.D. No.	AA-5	AA-6
Controls Emission of -	Adipic Acid Dust	HNO_3 & Adipic Acid
Scrubbing/Absorbing Liquid	Water	Water
Type - Spray	+	
Packed Column		+
Column w/trays		
Number of trays		
Kind of tray		
Plenum Chamber		
Other		
Scrubbing Absorbing Liquid Rate - GPM	5	3
Design Temp. (operating Temp.) F°	120	200
Gas Rate, SCFM (lb./hr.)	18,000	425
T-T Height, Ft.	15	5.25
Diameter, Ft.	10	2
Washed Gases to Stack -	No	Yes
Stack Height - Ft.		85
Stack Diameter - Inches		8
Installed Cost - Mat'l. & Labor - $	25,000	15,000
Installed Cost - Based on - "year" - Dollars	1960	1967
Installed Cost - ¢/lb. of Adipic Acid/Yr.		
Operating Cost - Annual, $ (1972)	3500	1500
Value of Recovered Product, $/Yr.	0	0
Net Operating Cost - Annual, $	3500	1500
Net Operating Cost - ¢/lb. of Adipic Acid		
Efficiency - % SE	90	90+
INCINERATION DEVICES		
EPA Code No. for plant using		
Flow Diagram (Fig. II) Stream I.D		
Device I.D. No.		
Type of Compound Incinerated		
Type of Device - Flare		
Incinerator		
Other		
Material Incinerated, SCFM (lb./hr.)		
Auxilliary Fuel Req'd (excl. pilot)		
Type		
Rate - BTU/hr.		
Device or Stack Height - Ft.		
Installed Cost - Mat'l. & Labor - $		
Installed Cost Based on "year" Dollars		
Installed Cost - ¢/lb. of Adipic Acid/yr		
Operating Cost - Annual - $ (1972)		
Operating Cost - ¢/lb. of Adipic Acid		
Efficiency - CCE - %		
Efficiency - SERE - %		

TABLE AA-IV
CATALOG OF EMISSION CONTROL DEVICES
ADIPIC ACID PRODUCTION VIA NITRIC ACID OXIDATION OF CYCLOHEXANONE/CYCLOHEXANOL

Page 3 of 4

	Adipic Acid Purification	'Finished' Product Operations Drying, Conveying, Melting, etc	
CYCLONES			
EPA Code No. for plant using		5-3	5-4
Flow Diagram (Fig. II) Stream I.D.		E.	E.
Device I.D. No.		AA-10	AA-11
Controls Emission of		Adipic Acid Dust	Adipic Acid Dust
T-T Height - Ft.			18
Diameter - Ft.			5.5
No. of Stages			
Installed Cost - Mat'l. & Labor - $		63,000	30,000
Installed Cost based on - "year" - $		1964 — 1966	1967
Installed Cost - ¢/lb. of Adipic Acid/Yr.		.0210	.0375
Operating Cost - Annual - $ (1972)			2000
Value of Recovered Product, $/Hr.			3300
Net Operating Cost, $/Yr.			- 1300
Net Operating Cost, ¢/Lb. of Adipic Acid			
Efficiency - % SE		100	93.8
BAG FILTERS			
EPA Code No. for plant using	5-3		
Flow Diagram (Fig. II) Stream I.D.	C. II. L.		
Device I.D. No.	AA-9		
Controls Emissions of	HNO_3 + Adipic Acid Dust		
Number of Compartments			
Number of bags per compartment			
Bag Cloth Material			
Total Bag Area - Ft^2			
Design (operating) Temp. - F°			
Design (operating) press - psig			
Installed Cost - Mat'l. & Labor, $	28,000		
Installed Cost Based on - "Year" - Dollars	1967		
Installed Cost, ¢/lb. of Adipic Acid/Yr.	.0093		
Operating Cost - Annual - $ (1972)			
Value of recovered product - $/yr.			
Operating Cost - Annual - $ (1972)			
Value of Recovered product - $/yr.			
Net Operating Cost - $/Yr.			
Net Operating Cost - ¢/lb. of Adipic Acid			
Efficiency - % SE	HNO_3 - 90%, Dust - 100%		

TABLE AA-IV
EXPLANATION OF NOTES
CATALOG OF EMISSION CONTROL DEVICES
ADIPIC ACID PRODUCTION

Page 4 of 4

I	This device consists of two identical scrubbers. Costs reported are total costs.
II	No note.
III	This device consists of three identical scrubbers. Costs reported are total costs.
IV	Device consists of dust scrubber and cyclone but no description given of either.

TABLE AA-V
NUMBER OF NEW PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity (1) 1980	Capacity to be Added	Economic Plant Size	Number Of New Units
1430	160	1270	1900	2200	930	150	6 - 7

Note:

General - All capacities in MM Lbs./Yr.

(1) 1980 capacity based on growth rate of 5.5% per year as predicted by Chem. Marketing, April 24, 1972.

TABLE AA-VI
EMISSION SOURCE SUMMARY

Pollutant	Source				Total
	Reactor Off-Gas	Product Purification and Nitric Acid Recovery	"Finished" Product Operations - Conveying, Drying, etc.	Fugitive Emissions	
Hydrocarbon				Negligible	0
Particulate		.00005	.00010		.00015
NO_x	.0037	.017			.0207
SO_x					0
CO	.00010				.00010

Note: Pollutant quantities in lb./lb. of adipic acid.

TABLE AA-VII
WEIGHTED EMISSION RATES

Chemical: Adipic Acid

Process: HNO_3 Oxidation

Increased Capacity by 1980: 930 MM Lbs./Yr.

Pollutant	Emissions Lb./Lb.	Increased Emissions MM Lbs./Yr.	Weighting Factors	Weighted Emissions MM Lbs./Yr.
Hydrocarbon	0	0	80	0
Particulate	.00015	.140	60	8.4
NO_x	.0207	19.25	40	770
SO_x	0	0	20	0
CO	.00010	.093	1	0.1
			Significant Emissions Index	778.5

Adiponitrile via Butadiene

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I. Introduction

Adiponitrile is an intermediate in the synthesis of nylon 6, 6; with this use alone accounting for over 90% of all adiponitrile production. Several routes to adiponitrile are available, but (in the U. S.) only three are utilized at the present time. Primary raw materials for the three routes are:

(1) Butadiene
(2) Adipic Acid
(3) Acrylonitrile

In terms of process capacity, the process utilizing butadiene is pre-eminent - and is the subject of this survey report.

Nitrogen oxides comprise the bulk of the air pollutants associated with the butadiene process; with the major portion of them arising from the incineration of nitrogenous waste materials. Of less importance, but still significant, are the various hydrocarbon emissions generated by the chlorination section of the plant. Additionally, several waste liquid streams are produced, the most important of these being the waste brine produced by the chlorobutene cyanation reaction. In general, air emissions from the subject process can be characterized as moderate.

The current U. S. adiponitrile production capacity - for the butadiene process - is estimated at 4.35×10^8 lbs./yr. 1980 capacity is estimated to be 8.45×10^8 lbs./yr.; assuming that the process maintains its present share of the industry's total capacity. However, the butadiene process operates from a narrow base, with only one producer utilizing it, and the premise upon which the 1980 estimate is based, may best be described as - tenuous.

In most of the petrochemical industry survey reports there is a brief 'process description' section. However, data sufficient to permit the provision of such information in this report are not availabe, most probably because a sole producer has better control over the dissemination of process information. Consequently, the following discussion of process chemistry is substituted.

II. Process Chemistry

The production of adiponitrile from butadiene involves four distinct reaction steps. They are:

I. Chlorination

$$CH_2 = CH-CH = CH_2 + Cl_2 \longrightarrow CH_2Cl - CHCl - CH = CH_2$$

	Butadiene	Chlorine	3, 4 - Dichloro-1-Butene
Mol. Wt.	54.09	70.91	125.00

This reaction will procede readily in either the liquid or gas phase and with or without a catalyst. It is believed that current commercial practice is restricted to a copper chloride catalyzed vapor phase process, with temperatures in the range of 150 to 350° C. Yields as low as 75% are reported by some of the earlier (Circa 1962) references available. A (perhaps) more realistic representation of commercial experience shows a (catalyzed) yield of 98%*, with the following distribution of useable isomers:

	3, 4 - Dichloro - 1 - Butene	42%
Cis	1, 4 - Dichloro - 2 - Butene	15%
Trans -	1, 4 - Dichloro - 2 - Butene	41%
		98%

II. Cyanation

$$CH_2Cl - CHCl - CH = CH_2 + 2\ NaCN \longrightarrow NC - CH_2 - CH(CN)-CH = CH_2 + 2\ NaCl$$

	3, 4 - Dichloro-1-Butene	Sodium Cyanide	3, 4 - Dicyano-1-Butene	Sodium Chloride
Mol. Wt.	125.00	49.01	106.13	58.45

The cyanation can be effected with either hydrogen cyanide or sodium cyanide, with the latter preferred. The reaction takes place in an aqueous media, and may be catalyzed with a cuprous cyanide complexing agent. The yield for this step, including extraction and distillation losses, is about 95%.

III. Isomerization

A

$$NC-CH_2-CH(CN)-CH = CH_2 \longrightarrow NC-CH_2-CH=CH-CH_2-CN$$

	3, 4 - Dicyano-1-Butene	1, 4 - Dicyano-2-Butene
Mol. Wt.	106.13	106.13

The above isomerization 'step' (III-A) apparently takes place more-or-less simultaneously with the cyanation 'step'. (Of course only about 40% of the dicyanobutenes formed undergo this re-arrangement since the other 60% were derived from dichlorobutenes of the 'proper' configuration - see Step I product distribution). The 1, 4 dicyano-2-butene so formed exists in both the cis and trans form. The trans form is a solid at processing conditions and some sources report that is is "partially isomerized to a liquid isomer". That reaction is shown below:

---

*Excluding processing losses.

B $NC{-}CH_2{-}CH = CH{-}CH_2{-}CN \longrightarrow NC{-}CH_2{-}CH_2{-}CH = CH{-}CN$

	(Trans only) 1, 4 - Dicyano-2-Butene	1, 4 - Dicyano-1-Butene
Mol. Wt.	106.13	106.13

Information regarding the process conditions favoring this isomerization (III-B) has not been found.

IV. Hydrogenation

$$NC{-}CH_2{-}CH = CH{-}CH_2{-}CN \quad + H_2 \longrightarrow NC{-}(CH_2)_4 - CN$$

	1, 4 - Dicyano-2-Butene	Hydrogen	Adiponitrile
Mol. Wt.	106.13	2.02	108.15

The mixture of 1, 4 dicyano-1-butene and 1, 4 dicyano-2-butene is hydrogenated over a palladium catalyst at 100° C to 300° C. An early reference states that at 25 atmospheres the yield is 96%.

III. Plant Emissions

A. Continuous Air Emissions

1. Chlorination Section Process Vents

The respondent reports three streams in this category. All contain butadiene and/or various chlorinated hydrocarbons. All three are relatively insignificant - with total emissions of approximately .002 lb./lb. of hydrocarbon.

2. Chlorination Section Storage Tank Vents

The two tank vents reported for this plant section are both nearly 100 percent nitrogen, and thus, essentially non-polluting.

3. Cyanide Snythesis Section Process Vents

This source contributes over 70 percent (on a weighted basis) of all the air emissions produced by the process. The vent consists of the combustion products from three incinerators and a boiler. In lieu of information to the contrary it has been assumed, that, upon combustion, 10 percent of the nitrogen in nitrogen containing compounds, is oxidized to NO_x. Emissions from this source are .0379 lbs./lb. of NO_x.

4. Cyanation and Isomerization Section Process Vents

Table IV summarizes the twelve streams reported by the respondent that fall into this category. Of the twelve, one contains a relatively small amount of NO_x (.021 lbs./lb.) and five contain varying (small) amounts of benzene, with a total benzene emission from this source of .008 lbs./lb. The other six streams contain only non-polluting substances; generally nitrogen, air or water vapor.

5. Cyanation and Isomerization Section Tank Vents

The two tank vents reported for this section of the plant both contain small amounts benzene. Total benzene from this source is approximately .0002 lbs./lb.

6. Hydrogenation Section Process Vents

The two vents reported from this section of the plant contain only insignificant amounts of ammonia and non-polluting compounds.

7. Boiler House Emissions

Waste liquids from the cyanation and isomerization section and from the hydrogenation section are burned as fuel. 2100 lbs./hr. of liquid containing 23.4 wt. percent nitrogen and 1.6 wt. percent chlorine and 11,000 lbs./hour of liquid containing 21.2 percent N_2 and 0.6 wt. percent chlorine are thus disposed of from these two sections. Emissions resulting from this operation amount to .00688 pounds aerosols (HCl) per pound and .05686 pounds NO_x per pound (assuming 10 percent of the nitrogen is oxidized to NO_x).

B. Intermittent Air Emissions

The respondent reports no intermittent air emissions.

C. Continuous Liquid Wastes

1. Waste Brine

1200 GPM of waste brine is produced. Disposal is by on-site deep well injection.

2. Spent Caustic

Although not reported as a liquid waste it would appear that a small amount of spent caustic would be produced through the operation of several gas scrubbing devices, which the operator has indicated do use caustic.

D. Solid Wastes

The operator reports disposal of 58,000 lb./month of waste solids via his plant land fill area. The solid waste includes 40,000 lb./month of miscellaneous trash such as packing material, waste paper etc. and 18,000 lb./month of 'chemical' waste such as filter aid, coke, polymer, etc.

E. Odors

In general the butadiene process for the production of adiponitrile does not appear to be a process that has an odor problem.

The respondent reported no odor complaints in the past year. Most of the reported odors are said to be detectable only on the plant property and only at intermittent intervals. The materials contributing to odors in this category have been identified as ammonia, chlorobutenes, chlorine, butadiene, benzene and triethylamine. However, according to the questionnaire, these emissions are well enough controlled to prevent odor problems.

F. Fugitive Emissions

In addition to storage tank vents, which have been listed elsewhere, two sources of fugitive emissions have been reported. The first is the chlorination section refrigeration unit, which 'loses' 1,700,000 lbs./yr. of propane. This is equal to .00531 lbs. of propane/lb. of adiponitrile. The second source, described as butadiene losses due to overloading the chlorination section recovery systems during start-ups and shut-downs, amounts to 3,400,000 lbs./yr. or .01062 lb./lb. No other significant source of fugitive emissions is thought to exist.

G. Other Emissions

The respondent reports that unknown quantities of emissions are associated with the following:

(1) Power House stacks.

(2) Cooling tower.

(3) Steam exhaust from flash tanks, turbines and reciprocating pumps.

(4) Exhuast from natural gas engines used to drive compressors.

IV. Emission Control

The emission control devices that have been reported as being employed by the operator of the butadiene process adiponitrile plant are summarily described in Table IV of this report. An efficiency has been assigned each device whenever data sufficient to calcualte it have been available. Three types of efficiencies have been calculated.

(1) "CCR" - Completeness of Combustion Rating

$$\text{CCR} = \frac{\text{Lbs. of } O_2 \text{ reacting (with pollutants in device feed)}}{\text{lb. of } O_2 \text{ that theoretically could react}} \times 100$$

(2) "SE" - Specific Efficiency

$$\text{SE} = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

(3) "SERR" - Significance of Emission Reduction Rating

$$\text{SERR} = \frac{\Sigma(\text{pollutant} \times \text{weighting factor})\text{in} - \Sigma(\text{pollutant} \times \text{weighting factor*})\text{ out}}{\Sigma(\text{pollutant} \times \text{weighting factor*})\text{in}} \times 100$$

*Weighting factor same as Table VII weighting factor.

Normally, a combustion type control device (i.e. incinerator, flare, etc.) will be assigned both a "CCR" and an "SERR" rating, whereas a non-combustion type device will be assigned an "SE" and/or an "SERR" rating. A more complete description of this rating method may be found in Appendix V of this report.

Although efficiency ratings for most devices are shown in Table IV, a few general comments regarding adiponitrile pollution control device performance seems in order:

Absorbers

Two thirds of the control devices reported consisted of, at least in part, some type of absorber. They are identified in Table IV as devices AN-4 to AN-12. With the exception of devices AN-5 and AN-7, all have calculated SE and SERR efficiencies of 100%. Absorber AN-5 is used in conjunction with a chiller and K. O. Drum. Its reported efficiency of 56.6% is the combined efficiency of both pieces of equipment. The specific efficiency, with regard to butadiene, is only 65%. Since butadiene is quite easy to absorb (efficiencies of 98 + % being common), one must assume that the particular device is either under-sized or was designed to perform at some economic optimum - rather than at much higher, though practical, hydrocarbon recovery rates. The other device with a low efficiency (AN-7 w/SE of 75%) appears to suffer from a poor choice of absorbents. More specifically, spent caustic does not seem to be the ideal absorbent for a mixture of butadiene, chloroprene and vinylcyclohexane - there may be other process considerations for this seemingly strange choice, but they have not been presented.

In summary, the performance of absorbers in adiponitrile pollution control applications is excellent, and in most instances their SE and SERR efficiencies approach 100%.

Incinerators

With one exception, the composition of flare or incinerator flue gases has not been reported. Consequently, efficiencies for these devices have been estimated (by Houdry) rather than calculated from actual performance data. This is necessary in order that an SEI (see Table VII) may be calculated. The estimated efficiencies are based on two assumptions:

I All hydrocarbons are completely combusted, producing only CO_2 and H_2O.

II Ten percent of the nitrogen in the combusted material is oxidized to NO_x, with a mol. wt. of 40.

The true efficiencies of these devices remain unknown.

It is extremely unlikely that a change in operating conditions will lead to a significant decrease in air pollution - considering the source of the major portion of the pollutants.

Development work directed toward reductions in emissions from this process falls into the following general categories.

(1) Substitute alternate disposal method for current practice of burning nitrogenous materials.

(2) More efficient design and operation of devices currently being utilized.

V. Significance of Pollution

It is recommended that no in-depth study of this process be undertaken at this time. The reported emission data indicate that the quantity of pollutants released as air emissions is less for the subject process than for other processes that are currently being surveyed.

The methods outlined in Appendix IV of this report have been used to estimate the total weighted annual emissions from these new plants. This work is summarized in Tables V, VI and VII.

Published support for the Table V forecast of new plants has not been found. The forecast is based on two assumptions:

(1) The butadiene process will account for 55.5 percent of 1980 adiponitrile capacity.

(2) Adiponitrile capacity in 1980 will be 111 percent of demand.

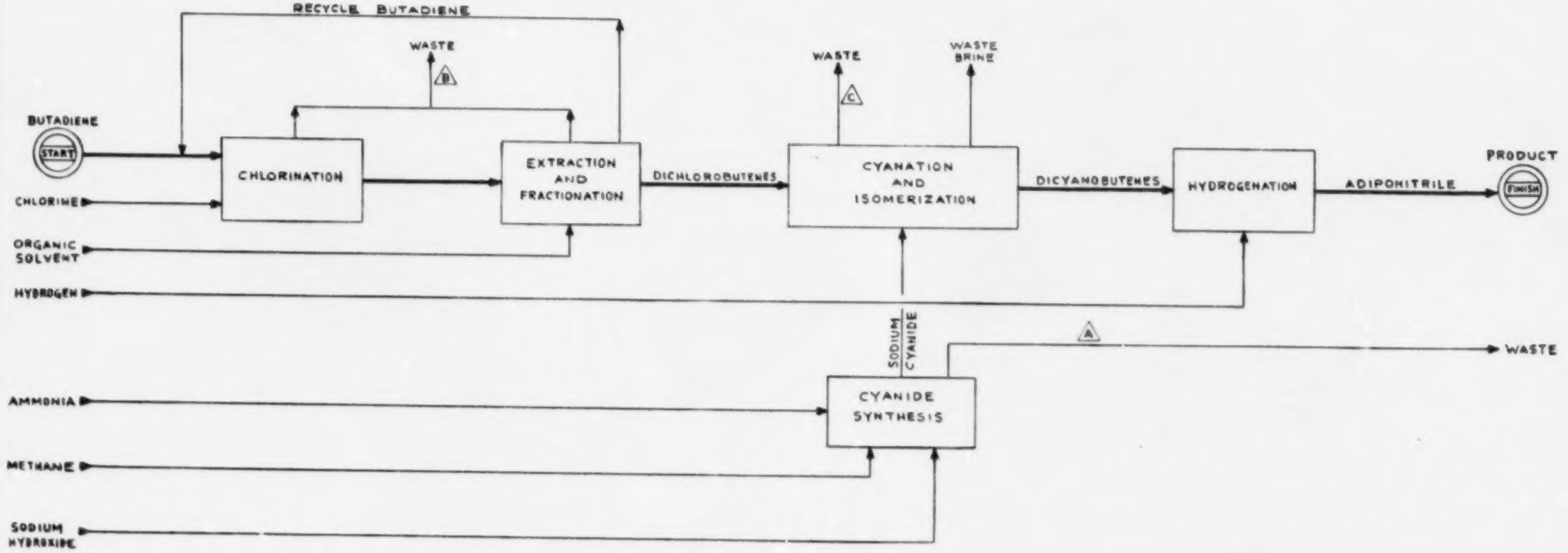
Unless there is a technological breakthrough it is believed that errors inherent in these assumptions will not significantly alter the SEI.

On a weighted emission basis a Significant Emission Index of 3,007 has been calculated in Table VII. This is less than the SEI's of many of the other processes in the study. Hence, the recommendation to exclude an in-depth study of adiponitrile production via the butadiene process from the in-depth study portion of the overall scope of work.

VI. Producers of Adiponitrile ex Butadiene

Apparently there is some question as to the location and capacity of the few plants utilizing the subject process. The capacities quoted below are, in part, based on assumptions outlined elsewhere in this report. Plant locations are based on published and private information.

Company	Location		1972 Capacity MM Lb./Yr.
Du Pont	Victoria, Texas		320
	La Place, Louisiana		115
		Total	435


BUTADIENE
START
CHLORINE
ORGANIC SOLVENT
HYDROGEN
AMMONIA
METHANE
SODIUM HYDROXIDE
RECYCLE BUTADIENE
WASTE
B
CHLORINATION
EXTRACTION AND FRACTIONATION
DICHLOROBUTENES
WASTE
C
WASTE BRINE
CYANATION AND ISOMERIZATION
SODIUM CYANIDE
CYANIDE SYNTHESIS
A
WASTE
DICYANOBUTENES
HYDROGENATION
ADIPONITRILE
PRODUCT
FINISH

NOTES:

1 LETTERED STREAMS ARE CROSS-REFERENCE IDENTITIES FOR CATALOG OF EMISSION CONTROL DEVICES - TABLE III

SCALE	NONE	DATE
DRAWN BY	E.C.A.	1-18-73
CHECKED BY	GBM	1-19-73
CATALYTIC APPROVAL		
CLIENT APPROVAL		2-2-73

FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO 68-02-0255

PREPARED BY
CATALYTIC, INC.
ENGINEERING DEPARTMENT, PHILADELPHIA, PENNA. 19102

FIGURE AN-1
BLOCK FLOW DIAGRAM
ADIPONITRILE FROM BUTADIENE

PROJECT NO. 42030
I.D. NO. 440
DWG. NO. R-211
REV. NO. A

TABLE AN-I
ADIPONITRILE
EX
BUTADIENE

MATERIAL BALANCE - T/T OF ADIPONITRILE

There are not sufficient published data available to permit the presentation of a meaningful material balance. The reader is referred to Section II - Process Chemistry - for more generalized information of this type.

TABLE AN-II
ADIPONITRILE
EX
BUTADIENE

GROSS HEAT BALANCE

There are not sufficient published data available to permit the construction of a heat balance for this process.

TABLE AN-III
NATIONAL EMISSIONS INVENTORY
ADIPONITRILE
EX
BUTADIENE

Page 1 of 6

Plant EPA Code No.		6-3		
Capacity, Tons of Adiponitrile/Yr		160,000		
Range in Production - % of Maximum		0		
Emissions to Atmosphere Stream	Fugitive Emiss. from Refrig. Unit	Cyanide Sect. Vent Inciner. Flue Gas	Chlorination Sect. By-Product Vent	Chlorination Sect Process Vent
Flow - Lbs./Hr.	1,700,000/Yr.	259,933	650	82
Flow Characteristic, Continuous or Intermittent	Intermittent	Continuous	Cortinuous	Continuous
if Intermittent, Hrs./Yr. - Flow				
Composition, Tons/Ton of Adiponitrile		(A)		
Propane	.00531			
Nitrogen		4.88321	.01356	.00071
Oxygen			.00069	
Carbon Monoxide				
Carbon Dioxide		.54403	.00362	
Water		1.33472		
NO_x		.37903		
Misc. Lt. HC				.00070
Butadiene				.00083
Chloroprene				
Vinyl Cyclohexane				
Benzene				
Hydrogen Chloride				
Hydrogen				
Methane				
Ammonia				
Vent Stacks	No	Yes	Yes	Yes
Number		4	1	1
Height - Ft.		164 140 175 90	65	90
Diameter - Inches		16 30 6.5 6	2	1.5
Exit Gas Temp. - F°		95	95	122
SCFM/Stack			144	
Emission Control Devices	None	AN-1 AN-2 AN-3 Yes	AN-4	AN-5
Flare/Incinerator		+ + +	+	
Refrig. Cond/K. O. Drum				+
Absorber/Scrubber			+	+
Other		+		
Analysis	None			
Date or Frequency of Sampling				
Sample Tap Location		None		
Type of Analysis		Calc'd.	Calc'd.	
Odor Problem	No	No	No	No
Summary of Air Pollutants				
Hydrocarbons, Ton/Ton of Adiponitrile		See Continuation		
Particulates, Ton/Ton of Adiponitrile				
NO_x, Ton/Ton of Adiponitrile				
SO_x, Ton/Ton of Adiponitrile				
CO , Ton/Ton of Adiponitrile				

TABLE AN-III
NATIONAL EMISSIONS INVENTORY
ADIPONITRILE
EX
BUTADIENE

Page 2 of 6

Plant EPA Code No.	D-3		
Capacity, Tons of Adiponitrile/Yr.	160,000		
Range in Production - % of Maximum	0		
Emissions to Atmosphere			
Stream	Chlorination Sect. Fugitive Emissions & Emergency Vents	Chlorination Sect. Storage Vent	Chlorination Sect. Vac. Ejector Disch.
Flow - Lbs./Hr	3,500,000/Yr	100	174
Flow Characteristic, Continuous or Intermittent	Intermittent	Continuous	Continuous
If Intermittent, Hrs./Yr. Flow			
Composition, Tons/Ton of Adiponitrile			
Propane			
Nitrogen		.00275	.00284
Oxygen			
Carbon Monoxide			
Carbon Dioxide			
Water			.00008
NO_x			
Misc. Lt. HC			
Butadiene	.01042		.00015
Chloroprene			.00022
Vinyl Cyclohexane			.00008
Benzene			
Hydrogen Chloride			
Hydrogen			
Methane			
Ammonia			
Vent Stacks	No	Yes	Yes
Number		1	1
Height - Ft.		90	90
Diameter - Inches		8	8
Exit Gas Temp. - F°		120	120
SCFM/Stack		23	26
Emission Control Devices	No	AN-6 (B)	AN-7 (B)
Flare/Incinerator			
Refrig. Cond/K. O. Drum			
Absorber/Scrubber		+	+
Other			
Analysis			
Date or Frequency of Sampling			
Sample Tap Location			
Type of Analysis	Calc'd	Calc'd	Calc'd.
Odor Problem	No	No	No
Summary of Air Pollutants			
Hydrocarbon, Ton/Ton of Adiponitrile		See Continuation	
Particulates, Ton/Ton of Adiponitrile			
NO_x, Ton/Ton of Adiponitrile			
SO_x, Ton/Ton of Adiponitrile			
CO_x, Ton/Ton of Adiponitrile			

TABLE AN-III
NATIONAL EMISSIONS INVENTORY
ADIPONITRILE
EX
BUTADIENE

Page 3 of 6

Plant EPA Code No. 6-3
Capacity, Tons of Adiponitrile/Yr. 160,000
Range in Production - % of Maximum 0

Emissions to Atmosphere Stream	Chlorination Section Storage Tank Vent	Cyanation & Isomerization Process Vent	C & I Process Vent	C & I Process Vent	C & I Ejector Effl.	C & I Process Vent	C & I Process Vent	C & I Process Vent
Flow - Lbs./Hr.	67	781	92	6429 (A)	35	2	36	36
Flow Characteristic, Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous
If Intermittent, Hrs./Yr. Flow								
Composition, Tons/Ton of Adiponitrile				(A)				
Propane								
Nitrogen	.00184				.00094	.00006	} .00013	} .00013
Oxygen								
Carbon Monoxide								
Carbon Dioxide		.02101		.12583				
Water		.00045	.00022	.02576				
NO_x				.02120				
Misc. Lt. HC								
Butadiene								
Chloroprene								
Vinyl Cyclohexane								
Benzene			.00230				.00086	.00086
Hydrogen Chloride				.00381				
Hydrogen								
Methane								
Ammonia								
Vent Stacks	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Number		1	1	1	1	1	1	1
Height - Ft.		70	55	175	90	65	90	90
Diameter - In.		6	3	6.5	6	2	1.5	1.5
Exit Gas Temp. - F°		140	158		95	95	122	122
SCFM/Stack		115			8	0.6	3.6	3.6
Emission Control Devices	AN-8 (C)	No	No	AN-3	AN-9	AN-10	No	No
Flare/Incinerator				+				
Refrig. Cond./K. O. Drum								
Absorber/Scrubber	+				+	+		
Other								
Analysis								
Date or Frequency of Sampling		Infrequently	Never	Never				
Sample Tap Locaton			None	None				
Type of Analysis		Wet	Calc'd	Calc'd				
Odor Problem			No	No	No			
Summary of Air Pollutants								
Hydrocarbons, Ton/Ton of Adiponitrile								
Particulates, Ton/Ton of Adiponitrile								
NO_x, Ton/Ton of Adiponitrile								
SO_x, Ton/Ton of Adiponitrile								
CO, Ton/Ton of Adiponitrile								

SEE CONTINUATION

TABLE AN-III
NATIONAL EMISSIONS INVENTORY
ADIPONITRILE
EX
BUTADIENE

Page 4 of 6

Plant EPA Code No.	6-3						
Capacity, Tons of Adiponitrile/Yr	160,000						
Range in Production - % of Maximum	0						
Emissions to Atmosphere							
Stream	C & I Vac. Ejector Disch.	C & I Process Vent	C & I Process Vent	C & I Process Vent	C & I Process Vent	C & I Tank Vents	C & I Tank Vents
Flow - lbs./Hr.	115	58	92	1353	92	5	7
Flow Characteristic, Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous
If Intermittent, Hrs./Yr. - Flow							
Composition, Tons/Ton of Adiponitrile							
Propane							
Nitrogen	.00316			.03718		.00009	
Oxygen		} .00159					
Carbon Monoxide							
Carbon Dioxide							
Water			.00022		.00022		.00007
NO_x							
Misc. Lt. HC							
Butadiene							
Chloroprene							
Vinyl Cyclohexane							
Benzene			.00230		.00230	.00003	.00016
Hydrogen Chloride							
Hydrogen							
Methane							
Ammonia							
Vent Stacks	No	No	Yes	Yes	Yes	No	No
Number			1	1	1		
Height - Ft.			25	30	25		
Diameter - Inches			3	2	3		
Exit Gas Temp. - F°			158	104	158		
SCFM/Stack				306			
Emission Control Devices	No	AN-11 (D)	No	AN-12 (D)	No	No	No
Flare/Incinerator							
Refrig. Cond./K. O. Drum							
Absorber/Scrubber		+		+			
Other							
Analysis							
Date or Frequency of Sampling							
Sample Tap Location							
Type of Analysis							
Odor Problem							
Summary of Air Pollutants							
Hydrocarbons, Ton/Ton of Adiponitrile				SEE CONTINUATION			
Particulates, Ton/Ton of Adiponitrile							
NO_x, Ton/Ton of Adiponitrile							
SO_x, Ton/Ton of Adiponitrile							
CO, Ton/Ton of Adiponitrile							

TABLE AN-111
NATIONAL EMISSIONS INVENTORY
ADIPONITRILE
EX
BUTADIENE

Plant EPA Code No.		n-3	
Capacity, Tons of Adiponitrile/Yr.		160,000	
Range in Production - of Maximum		0	
Emissions to Atmosphere			
Stream	Hydrogenation Unit Process Vent		Hydrogenation Unit Ejector Discharge
Flow - lbs./Hr.	2.1		384
Flow Characteristic, Continuous or Intermittent	Continuous		Continuous
if Intermittent, Hrs./Yr. - Flow			
Composition, Tons/Ton of Adiponitrile			
Propane			
Nitrogen			.01054
Oxygen			
Carbon Monoxide			
Carbon Dioxide			
Water			
NO_x			
Misc. Lt. HC			
Butadiene			
Chloroprene			
Vinyl Cyclohexane			
Benzene			
Hydrogen Chloride			
Hydrogen	.00180		
Methane	.00477		
Ammonia	.00004		
Vent Stacks	No		No
Number			
Height - Ft.			
Diameter - Inches			
Exit Gas Temp. - F°			
SCFM/Stack			
Emission Control Devices	No		No
Flare/Incinerator			
Refrig. Cond./K. O. Drum			
Absorber/Scrubber			
Other			
Analysis			
Date or Frequency of Sampling			
Sample Tap Location			
Type of Analysis			
Odor Problem			
Summary of Air Pollutants			
Hydrocarbons, Ton/Ton of Adiponitrile		.02564	
Particulates, Ton/Ton of Adiponitrile		.00385	
NO_x, Ton/Ton of Adiponitrile		.40023	
SO_x, Ton/Ton of Adiponitrile			
CO, Ton/Ton of Adiponitrile			

TABLE AN-III
NATIONAL EMISSIONS INVENTORY
ADIPONITRILE
EX
BUTADIENE

EXPLANATION OF NOTES

Page 6 of 6

(A) Respondent reported composition of stream prior to combustion. Combustion products estimated by Houdry.

(B) Devices AN-6 and AN-7 both consist of three identical scrubbers.

(C) Device AN-8 consists of six identical scrubbers.

(D) Devices AN-11 and AN-12 consist of two identical scrubbers.

TABLE AN-IV
CATALOG OF EMISSION CONTROL DEVICES
ADIPONITRILE EX BUTADIENE

Page 1 of 4

	CYANIDE SYNTHESIS			CHLORINATION (II)
ABSORBERS/SCRUBBERS				
EPA Code No. for plant using				6-3
Flow Diagram (Fig. 1) Stream I. D.				△
Device I. D. No.				AN-4
Control Emission of				Chlorinated HC
Scrubbing/Absorbing Liquid				Water
Type - Spray				
Packed Column				
Column w/trays				
Number of Trays				
Tray Type				
Other				Shell & Tube
Scrubbing/Absorbin Liquid Rate - GPM				
Design Temp. (Operating Temp.) F°				200
Gas Rate, SCFM (Lb./Hr.)				144
T-T Height, Ft				25 - 27
Diameter, Ft.				6 - 7
Washed Gases to Stack				Yes
Stack Height - Ft.				65
Stack Diameter - Inches				2
Installed Cost - Mat'l. & Labor - $				4,120,000
Installed Cost Based on - "year" - dollars				1963 - 1972
Installed Cost - ¢/lb. of Adiponitrile - Yr.				1,28750
Operating Cost - Annual, $ (1977)				776,000
Value of Recovered Product, $/Yr				925,000
Net Operating Cost - Annual, $				-149,000
Net Operating Cost - ¢/lb. of Adiponitrile				Negative
Efficiency - % - SE				100
Efficiency - % - SERR				100
INCINERATION DEVICES				(II)
EPA Code No. for plant using	6-3	6-3	6-3	6-3
Flow Diagram (Fig. 1) Stream I. D.	△	△	△	△
Device I. D. No.	AN-1	AN-2	AN-3	AN-4
Type of Compound Incinerated	Lt. HC, NH_3, HCN	Lt. HC, NH_3, HCN	Lt. HC, NH_3, HCN	Chlorinated HC
Type of Device - Flare	+	+		
Incinerator			+	+
Other				
Material Incinerated, SCFM (lb./hr.)	833	5833	5833	
Auxiliary Fuel Req'd. (excl. pilot)	Yes	Yes	Yes	Yes
Type	Nat. Gas	Nat. Gas	Nat. Gas	Hydrogen
Rate - BTU/Hr.	75 CFH	350 CFH	5000 CFH	672 CFH
Device or Stack Height - Ft.	164	140	175	65
Installed Cost - Mat'l. & Labor - $	12,770	48,900	386,700	4,120,000
Installed Cost Based on - "year" - dollars	1950	1958	1950 - 1968	1963 - 1972
Installed Cost - ¢/lb. of Adiponitrile - Yr.	.00399	.01528	.12084	1.2875
Operating Cost - Annual - $ (1977)		160,700		-149,000 (Net)
Operating Cost - ¢/lb. of Adiponitrile		.05021		Negative
Efficiency - % - CCR	100	100	100	100
Efficiency - % - SERR	~95 (I)	~95 (I)	~95 (I)	100

TABLE AN-IV
CATALOG OF EMISSION CONTROL DEVICES
ADIPONITRILE EX BUTADIENE

Page 2 of 4

CHLORINATION

ABSORBERS/SCRUBBERS	(III)			(IV)
EPA Code No. for plant using	6-3	6-3	6-3	6-3
Flow Diagram (Fig. 1) Stream I. D.	△ [illegible]	△ [illegible]	△ [illegible]	△ [illegible]
Device I. D. No.	AN-5	AN-6	AN-7	AN-8
Control Emission of	Butadiene & Lt. HC	Chlorinated HC	Chlorinated HC	Chlorinated HC
Scrubbing/Absorbing Liquid	Oil	Spent Caustic	Spent Caustic	Water
Type - Spray	Not Specified	Not Specified	Not Specified	
Packed Column				
Column w/trays				
Number of Trays				
Tray Type				
Other				
Scrubbing/Absorbing Liquid Rate - GPM				12
Design Temp. (Operating Temp.) F°		(120)	(120)	(Ambient)
Gas Rate, SCFM (lb./Hr.)		22.7	26	15
T-T Height, Ft.		~14	~14	
Diameter, Ft.		~2	~2	3
Washed Gases to Stack	Yes	Yes	Yes	No
Stack Height - Ft.	90	90	90	
Stack Diameter - In.	1.5	8	8	
Installed Cost - Mat'l. & Labor - $	50,000	14,500	14,500	12,000
Installed Cost Based on - "year" - dollars	1950 - 1971	1953	1953	1962
Installed Cost - $/lb. of Adiponitrile - Yr.	.01562	.00453	.00453	.00375
Operating Cost - Annual, $ (1972)	5,500	1,300	1,300	14,600
Value of Recovered Product, $/Yr.	425,000	0	0	0
Net Operating Cost - Annual, $	-419,500	1,300	1,300	14,600
Net Operating Cost - $/lb. of Adiponitrile	Negative	.00040	.00040	.00456
Efficiency - % - SE	56.6	~100	74.6	100
Efficiency - % - SERR	56.6	~100	74.6	100

TABLE AN-IV
CATALOG OF EMISSION CONTROL DEVICES
ADIPONITRILE EX BUTADIENE

ABSORBERS/SCRUBBERS				
EPA Code No. for plant using	6-3	6-3	(V) 6-3	(V) 6-3
Flow Diagram (Fig. 3) Stream I. D.	C.	C.	C.	C.
Device I. D. No.	AN-9	AN-10	AN-11	AN-12
Control Emission of	Tetra-Ethyl Amine	Tetra-Methyl Amine	HCN	HCN
Scrubbing/Absorbing Liquid	Water	Water	12% NaOH	12% NaOH
Type - Spray				
Packed column	+	+	+	+
Column w/trays				
Number of trays				
Tray type				
Other				
Scrubbing/Absorbing Liquid Rate - GPM	5	0.5		
Design Temp. (Operating Temp.) F°	(95)	(95)	(158)	(104)
Gas Rate, SCFM (Lb./Hr.)	8	0.7	167	306
T-T Height, Ft.	39	10.5	9.8	8
Diameter, Ft.	2	0.5	0.7	0.7
Washed Gases to Stack	Yes	Yes	No	Yes
Stack Height - Ft.	90	65		30
Stack Diameter - In.	[illegible]	2		2
Installed Cost - Mat'l. & Labor - $	44,000	3,000	3,000	3,000
Installed Cost Based on - "year" - dollars	1970			
Installed Cost - ¢/lb. of Adiponitrile - Yr.	.01375	.00093	.00093	.00093
Operating Cost - Annual, $ (1972)	10,400	580	9030	9030
Value of Recovered Product, $/Yr.	0	0	0	0
Net Operating Cost - Annual, $	10,400	580	9030	9030
Net Operating Cost - ¢/lb. of Adiponitrile	.00325	.00018	.00282	.00282
Efficiency - % - SE	~100%	~100%	~100%	~100%
Efficiency - % - SERP	~100%	~100%	~100%	~100%

TABLE AN-IV
CATALOG OF EMISSION CONTROL DEVICES
ADIPONITRILE
EX
BUTADIENE

EXPLANATION OF NOTES

I. When respondent does not report composition of combustion products, it is assumed that ten percent of the nitrogen in all nitrogenous compounds is oxidized to NO_x.

II. Device AN-4 is a combination incinerator/absorber/scrubber. Operating and installed cost figures shown are for the entire device. Performance efficiencies also refer to the overall performance of the device.

III. Device AN-5 used in conjunction with propane chiller.

IV. Device AN-8 consists of six identical scrubbers.

V. Device consists of two identical scrubbers.

TABLE AN-V
NUMBER OF NEW PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand* 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
435	0	435	760	845	410	100	4

Note: All capacities in MM Lbs./Yr.

*Based on assumption that butadiene process will account for 55.5% of adiponitrile production.

Total adiponitrile demand based on C. E. H. and Chem. Systems estimates of HMDA demand.

TABLE AN-VI
EMISSION SOURCE SUMMARY
TON/TON OF ADIPONITRILE

Emission	Source*					Total
	Chlorination	Cyanide Synthesis	Cyanation and Isomerization	Hydrogenation	Boiler House Combustion of Liquid Waste	
Hydrocarbons	.01791		.00773			.02564
Particulates & Aerosols			.00381	.00004	.00688	.01073
NO_x		.0379	.02120		.05686	.11596
SO_x						
CO						

*Emissions from individual sections include fugitive emissions.

TABLE AN-VII
WEIGHTED EMISSION RATES

Chemical Adiponitrile

Process Butadiene

Increased Capacity by 1980 410 MM Lb./Yr.

Pollutant	Emissions, Lb./Lb.	Increased Emissions MM Lbs./Yr.	Weighting Factor	Weighted Emissions MM Lbs./Yr.
Hydrocarbons	.02564	10.51	80	841
Aerosols	.01073	4.40	60	264
NO_x	.11596	47.54	40	1,902
SO_x	0	0	20	0
CO	0	0	1	0
			Significant Emission Index	= 3,007

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I. Introduction

Adiponitrile is an intermediate in the synthesis of nylon 6,6; with this use alone accounting for over 90% of all adiponitrile production. Several routes to adiponitrile are available, but (in the U. S.) only three are utilized at the present time. Primary raw materials for the three routes are:

(1) Butadiene
(2) Adipic Aicd
(3) Acrylonitrile

In terms of production capacity, the adipic acid process is pre-eminent in Europe and second ranked in the United States. That process is the subject of this report.

Nitrogen compounds, more specifically NH_3 and NO_x, comprise the sum total of air pollutants associated with the adipic acid process. Some tars are produced, but they are disposed of by land fill methods and do not contribute to air pollution. Additionally, several waste water streams are produced. In general, air emissions from the subject process - based on information supplied by the petrochemical questionnaire respondents - are very low.

The current U. S. adiponitrile ex adipic acid production capacity is 2.80×10^8 lbs./yr. 1980 capacity is estimated to be 5.50×10^8 lbs./yr. - assuming that the subject process maintains its present share of the industry's total capacity.

II. Process Description

Adipic acid, in the presence of a dehydrating catalyst, reacts with ammonia to form adiponitrile. The chemical reaction is:

$$HOOC\,(CH_2)_4\,COOH + 2\,NH_3 \longrightarrow NC\,(CH_2)_4\,CN + 4\,H_2O$$

$$\text{Adipic Acid} + \text{Ammonia} \longrightarrow \text{Adiponitrile} + \text{Water}$$

$$\text{Mol. Wt.}\quad 146.14 \qquad 17.03 \qquad\qquad 108.15 + 18.02$$

Standard commercial practice is to conduct the reaction in the vapor phase, utilizing a phosphorous containing compound as the catalyst.

Adipic acid is melted, heated to between 500 - 600° F and sparged into the bottom of the number one reactor. In the reactor, the molten adipic acid vaporizes and mixes with an excess of ammonia, which has also been sparged in. The vapors pass up through reactor tubes packed with a mixture of phosphoric acid and bone particles. The reactor effluent is cooled 75 - 100 F° and sent to a vapor/liquid separator. The liquid from the separator is sent to reactor No. 2, where it is revaporized and contacted with additional ammonia. The tars and heavy ends formed in reactor No. 2 are rejected and the remainder of the reaction products are combined with the vapor phase effluent from reactor No. 1. The combined effluents pass on to the ammonia still where ammonia, carbon dioxide and water are taken overhead; crude adiponitrile is taken as a 'middle cut' and unreacted adipic acid is taken as a bottoms product. The ammonia overhead product is purified and recycled. The bottoms are returned to reactor No. 1.

The crude adiponitrile, from the ammonia still 'middle cut', is processed in a series of columns which dehydrate it and remove light and heavy ends. Product adiponitrile is sent to storage, where it is maintained at 105 - 110° F until it is used.

III. Plant Emissions

A. Continuous Air Emissions

1. Ammonia Recovery Section Vent

Both respondents report atmospheric emissions from this source. The operator of plant EPA Code No. 6-1 burns these materials in his plant flare. Estimated noxious emissions, based on the assumption that ten percent of N becomes NO_x, amount to .00027 lbs. NO_x/lb. of adiponitrile and constitutes the total amount of air pollutants emitted by the plant. The operator of plant EPA Code No. 6-2 reports the use of an absorber/scrubber (device AL-2, Table IV) on this stream. This device operates with an efficiency approaching 100 percent and pollutant emission is essentially nil.

2. Product Fractionation Vent

Both respondents report atmospheric emissions from this source. The operator of plant EPA Code No. 6-1 burns these materials in a "thermal oxidizer" (device AL-1, Table IV) and reports only trace emissions of NO_x in the flue gas. The operator of plant EPA Code No. 6-2 reports only "trace" flow from this source, with 99 percent of the "trace" flow - water and 'trace' amounts of NO_x.

3. Product Recovery Vent

Plant operator 6-2 reports discharging .0036 lbs./lb of ammonia from vacuum ejectors located in this area of his plant. According to his report this emission constitutes his only significant release of atmospheric pollutants. All reported streams are summarized in Table III.

B. Intermittent Air Emissions

No intermittent air emissions were reported.

C. Continuous Liquid Wastes

Waste water in the amount of 16 GPM is 'treated and disposed' by plant 6-1. Plant 6-2 allocates its waste water production as follows:

NH_3 Recovery	250 GPM
Purification	30 GPM
Product Recovery & Refining	5 GPM
Total -	285 GPM

All 285 GPM are subject to "in-plant treating and processing".

No other liquid waste streams were reported.

D. Solid Wastes

The operator of plant EPA Code No. 6-1 reports the production of 10,400 lbs./day of solid wastes. The wastes are 'disposed' of by "piling them" on the plant site. Plant 6-2 operator reports disposing of 12,000 lbs./day of waste solids by landfill on plant property. The solid wastes consist, in part, of spent catalyst. Other components were not identified.

E. Odors

In general, the adipic acid process for the production of adiponitrile does not appear to be a process that has an odor problem.

Both respondents reported no odor complaints in the past year. In fact, neither respondent admitted to the detection of any odors, at any time - even on plant property. Despite this fact, it seems only reasonable to expect the occassional presence of ammonia odors - at least on the plant site.

F. Fugitive Emissions

Neither respondent offers an estimate of fugitive losses. The operator of plant 6-2 summarizes the situation thusly: "NH_3 handling has the highest potential for possible emissions due to leaks. Since ammonia is readily detectable, leaks are promptly corrected and do not represent any appreciable loss".

G. Other Emissions

The only candidate for inclusion in this category would be the 0.02% sulfur in the natural gas reported by operator 6-2. However, this amounts to only one ton/yr. of sulfur, and is, therefore, insignificant.

IV. Emission Control

The emission control devices that have been reported as being employed by the operators of the adipic acid process adiponitrile plants are summarily described in Table IV of this report. An efficiency has been assigned each device whenever data sufficient to calculate it have been available. Three types of efficiencies have been calculated.

(1) "CCR" - Completeness of Combustion Rating

$$\text{CCR} = \frac{\text{lbs. of } O_2 \text{ reacting (with pollutants in device feed)}}{\text{lbs. of } O_2 \text{ theoretically capable of reacting}} \times 100$$

(2) "SE" - Specific Efficiency

$$\text{SE} = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

(3) "SERR" - Significance of Emission Reduction Rating

$$\text{SERR} = \frac{\sum(\text{pollutant} \times \text{weighting factor}^*)\text{in} - \sum(\text{pollutant} \times \text{weighting factor}^*)\text{out}}{\sum(\text{pollutant} \times \text{weighting factor}^*)\text{in}} \times 100$$

*Weighting factor same as Table VII weighting factor.

Normally a combustion type control device (i.e. incinerator, flare, etc.) will be assigned both a "CCR" and an "SERR" rating, whereas a non-combustion type device will be assigned as "SE" and/or an "SERR" rating. A more complete description of this rating method may be found in Appendix V of this report.

Although efficiency ratings for all (both) devices reported are shown in Table IV, a few general comments regarding adiponitrile pollution control device performance seems in order:

Absorbers/Scrubbers

Device AL-2 is a combination absorber/scrubber. It is the only device reported that belongs in the subject category. It is used to prevent the emission of ammonia. Based on the infomation supplied by the operator utilizing the device its efficiency (SE & SERR) is 100%.

Incinerators

The operator of plant EPA Code No. 6-1 utilizes two combustion devices for pollution control; the plant flare and an incinerator. The incinerator, a John Zink Thermal Oxidizer, is identified as device AL-1 in Table IV. Based on flue gas analyses, this device is capable of converting all contained nitrogen to N_2, and hence, its efficiency (CCR & SERR) is 100%. On the other hand, no information is given on the performance of the flare. However; in order to calculate an SEI (see Table VII), its performance or efficiency must be estimated. The efficiency estimate is based on two assumptions:

I All hydrocarbons are completely combusted, producing only CO_2 and H_2O.

II The nitrogen in the combusted material is oxidized to NO_x, with a mol. wt. of 40.

Thus, the effluent composition of the device was calculated and listed in Table III.

Based on the information supplied by the two respondents, emissions are already so low that further work in emission control seems unnecessary at this time.

V. Significance of Pollution

It is recommended that no in-depth study of this process be undertaken. The reported emission data indicate that the quantity of pollutants released as air emissions is less for the subject process than for many other processes studied to date.

The methods outlined in Appendix IV of this report have been used to estimate the total weighted annual emissions from these new plants. This work is summarized in Tables V, VI and VII.

Published support for the Table V forecast of new plants has not been found. The forecast is based on two assumptions:

(1) The adipic acid process will account for 36 percent of 1980 adiponitrile capacity.

(2) Adiponitrile capacity in 1980 will be 111 percent of demand.

Errors inherent in these assumptions, unless they are several orders of magnitude in size, cannot significantly alter the SEI.

On a weighted emission basis, a Significant Emission Index of 30 has been calculated for the subject process. This is substantially lower than the SEI of most of the processes studied. Hence, the recommendation to exclude an in-depth study of adiponitrile production via the adipic acid process from the in-depth study portion of the overall scope of work.

VI. Producers of Adiponitrile ex Adipic Acid

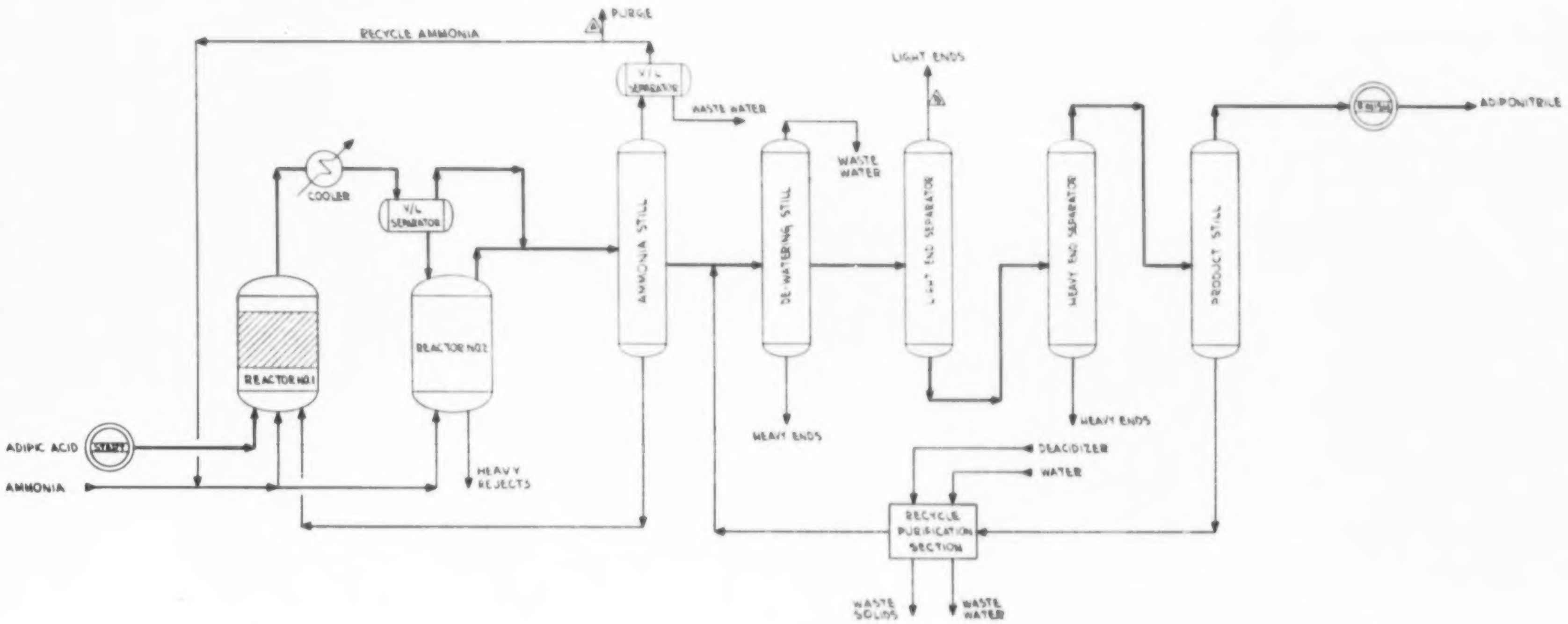
The capacities and plant locations listed below are based on information provided in the questionnaires and in the literature.

Company	Location	Capacity 1967	Capacity 1972
Celanese Corp.	Bay City, Texas	45	?
El Paso Products	Odessa, Texas		27.5
Monsanto	Pensacola, Florida		180
	Est. Total		280

Note:

(1) Capacities in MM Lbs./Yr.

(2) Estimated 1972 capacity based in part on assumptions outlined in Section V of this report.


RECYCLE AMMONIA
A
PURGE
V/L SEPARATOR
WASTE WATER
LIGHT ENDS
B
ADIPONITRILE
FINISH
COOLER
V/L SEPARATOR
AMMONIA STILL
DE-WATERING STILL
WASTE WATER
LIGHT END SEPARATOR
HEAVY END SEPARATOR
PRODUCT STILL
REACTOR NO.1
REACTOR NO.2
ADIPIC ACID
START
AMMONIA
HEAVY REJECTS
HEAVY ENDS
HEAVY ENDS
DEACIDIZER
WATER
RECYCLE PURIFICATION SECTION
WASTE SOLIDS
WASTE WATER

NOTES

1. STREAMS IDENTIFIED BY LETTER (i.e. A) ARE REFERENCES TO ENTRIES IN TABLE IV - CATALOG OF EMISSION CONTROL DEVICES.

SCALE	NONE	DATE
DRAWN BY	HMP	2-5-75
CHECKED BY	RBM	2-6-75
CATALYTIC APPROVAL		
CLIENT APPROVAL	JWP	2-9-75

FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO 68-02-0255

PREPARED BY
CATALYTIC, INC.
ENGINEERING DEPARTMENT, PHILADELPHIA, PENNA. 19102

FIGURE AL-1
SIMPLIFIED FLOW DIAGRAM
ADIPONITRILE FROM ADIPIC ACID

PROJECT NO 42030
DWG NO R-215
REV NO A
441

TABLE AL-I
ADIPONITRILE
EX
ADIPIC ACID

MATERIAL BALANCE - T/T OF ADIPONITRILE

There are not sufficient published data available to permit the presentation of a meaningful material balance.

TABLE AL-II
ADIPONITRILE
EX
ADIPIC ACID

GROSS REACTOR HEAT BALANCE

There are not sufficient published data available to permit the construction of a detailed heat balance for this process. An estimate of the total reactor heat flow shows:

Heat In*	BTU/Lb. of Adiponitrile
Sum of steam, fired heaters and heat exchange	1490
Heat Out	
Endothermic heat of reaction	434
Differential enthalpy (Reaction products - feed)	1056
	1490

---

*w/60° temperature base.

TABLE AI-III
NATIONAL EMISSIONS INVENTORY
ADIPONITRILE
EX
ADIPIC ACID

Plant EPA Code No.	6-1		6-2		
Capacity, Tons of Adiponitrile/Yr.	13,750		90,000		
Range in Production - % of Max.	0		0		
Emissions to Atmosphere					
Stream	NH$_3$ Recovery Section Purge	Light Ends Incinerator Flue Gas	NH$_3$ Recovery Section Vent	Product Purification Vent	Product Recovery Ejector Discharge
Flow - Lbs./Hr.	70	49,510	209	"Trace"	1380
Flow Characteristic, Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous
If Intermittent, Hrs./Yr. Flow					
Composition, Tons/Ton of Adiponitrile	(A)				
Ammonia			+		.00356
Nitrogen	+	10.9706			).0133
Oxygen		2.33098			)
Carbon Dioxide	+	.60096	.00928		
Water	.0018)	.49169		+	.04444
Nitrogen Oxides	.000274	+		+	
Vent Stacks	(Flare)	Yes	Yes	Yes	Yes
Number		1	1	1	1
Height - Ft.		13	77	77	120
Diameter - Inches		57	4	5	2
Exit Gas Temp. - F°		1800	77°	212°	212
SCFM/Stack		11,000	~30		420
Emission Control Devices	Yes	Yes AI-1	Yes AL-2	No	No
Flare/Incinerator	+	+			
Absorber/Scrubber			+		
Condenser/K. O. Drum					
Other					
Analysis					
Date or Frequency of Sampling	1968	Never	Never	Never	Never
Sample Tap Location	Vent Line		None	None	None
Type of Analysis	GLC	Calc'd.	Estimate	Estimate	Estimate
Odor Problem	No	No	No	No	No
Summary of Air Pollutants					
Hydrocarbons, Ton/Ton of Adiopnitrile	0		0		
Aerosols " " " "	0		.00356		
NO$_x$ " " " "	.000274		0		
SO$_x$ " " " "	0		0		
CO " " " "	0		0		

(A) Assumed combustion products. Respondent report [illegible] and composition of stream prior to combustion (in flare). Combustion products were estimated by assuming 100 percent combustion and ten percent conversion of contained nitrogen to NO$_x$ with mol. wt. of 40.

TABLE AL-IV
CATALOG OF EMISSION CONTROL DEVICES
ADIPONITRILE EX ADIPIC ACID

	AMMONIA RECOVERY SECTION	PRODUCT FRACTIONATION SECTION
ABSORBER/SCRUBBERS		
EPA Code No. for plant using	6-2	
Flow Diagram (Fig.1) Stream I.D.	A	
Device I. D. No.	AL-2 (I)	
Control Emission of	Ammonia	
Scrubbing/Absorbing Liquid	Water	
Type - Spray		
Packed Column	+	
Column w/Trays		
Number of Trays		
Tray Type		
Other		
Scrubbing/Absorbing Liquid Rate - GPM	40	
Design Temp. (Operating Temp.) F°	(77)	
Gas Rate, SCFM (lb./hr.)	14	
T-T Height, Ft.	6.5	
Diameter, Ft.	2	
Washed Gases to Stack	Yes	
Stack Height - Ft.	77	
Stack Diameter - In.	4	
Installed Cost - Mat'l. & Labor - $	20,000	
Installed Cost Based on - "year" - dollars	1953 & 1956	
Installed Cost - ¢/lb. of Adiponitrile/Yr.	.0111	
Operating Cost - Annual, $ (1972)	2,000	
Value of Recovered Product, $/Yr.	0	
Net Operating Cost - ¢/lb. of Adiponitrile	.0011	
Efficiency - % - SE	100	
Efficiency - % - SERR	100	
INCINERATION DEVICES		
EPA Code No. for plant using		6-1
Flow Diagram (Fig. 1) Stream I.D.		B
Device I. D. No.		AL-1
Type of Compound Incinerated		Nitriles & Imines
Type of Device - Flare		
Incinerator		+
Other		
Material Incinerated, SCFM (lb./hr.)		(50)
Auxiliary Fuel Req'd. (Excl. pilot)		Yes
Type		Nat. Gas
Rate BTU/Hr.		130 MMCF/Yr.
Device or Stack Height - Ft.		13
Installed Cost - Mat'l. & Labor - $		80,000 (II)
Installed Cost Based on - "year" - dollars		1965
Installed Cost - ¢/lb. of Adiponitrile - Yr.		.2909
Operating Cost - Annual - $ (1972)		67,000
Operating Cost - ¢/lb. of Adiponitrile		.2436
Efficiency - % - CCR		100
Efficiency - % - SERR		100

(I) Device AL-2 consists of five identical scrubbers. Indicated costs are total costs.

(II) Installed cost estimated by Houdry. Respondent reported cost, excluding labor, of $41,265.

TABLE AL-V
NUMBER OF NEW PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand* 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
280	0	280	495	550	270	100	2 - 3

Note: All capacities in MM Lbs./Yr.

*Based on assumption that adipic acid process will account for 36% of adiponitrile production.

Total adiponitrile demand based on C.E.H. and Chem. Systems estimates of HMDA demand.

TABLE AL-VI
EMISSION SOURCE SUMMARY
TON/TON OF ADIPONITRILE

Emission	Source			Total
	Ammonia Recovery Section	Product Fractionation Section	Fugitive Emissions	
Hydrocarbons				
Particulates & Aerosols		.00178		.00178
NO_x	.000137		Negligible	.000137
SO_x				
CO				

TABLE AI-VII
WEIGHTED EMISSION RATES

Chemical Adiponitrile

Process Adipic Acid

Increased Capacity by 1980 270 MM Lb./Yr.

Pollutant	Emissions Lb./Lb.	Increased Emissions MM Lbs./Yr.	Weighting Factor	Weighted Emissions MM Lbs./Yr.
Hydrocarbons	0	0	80	0
Aerosols	.00178	.5	60	28.8
NO_x	.000137	.04	40	1.5
SO_x	0	0	20	0
CO	0	0	1	0

Significant Emission Index = 30.3

APPENDIX I

FINAL ADDRESS LIST

Air Products & Chemicals, Inc.
P. O. Box 97
Calvert City, Kentucky

Attention: Mr. Howard Watson

Allied Chemical Corp.
Morristown, New Jersey

Attention: Mr. A. J. VonFrank
Director Air & Water
Pollution Control

American Chemical Corp.
2112 E. 223rd
Long Beach, California 90810

Attention: Mr. H. J. Kandel

American Cyanamid Company
Bound Brook, New Jersey

Attention: Mr. R. Phelps

American Enka Corporation
Enka, North Carolina 28728

Attention: Mr. Bennet

American Synthetic Rubber Corp.
Box 360
Louisville, Kentucky 40201

Attention: Mr. H. W. Cable

Amoco Chemicals Corporation
130 E. Randolph Drive
Chicago, Illinois

Attention: Mr. H. M. Brennan, Director
of Environomental Control Div.

Ashland Oil Inc.
1409 Winchester Ave.
Ashland, Kentucky 41101

Attention: Mr. O. J. Zandona

Borden Chemical Co.
50 W. Broad Street
Columbus, Ohio 43215

Attention: Mr. Henry Schmidt

Celanese Chemical Company
Box 9077
Corpus Christi, Texas 78408

Attention: Mr. R. H. Maurer

Chemplex Company
3100 Gulf Road
Rolling Meadows, Illinois 60008

Attention: Mr. P. Jarrat

Chevron Chemical Company
200 Bush Street
San Francisco, California 94104

Attention: Mr. W. G. Toland

Cities Service Inc.
70 Pine Street
New York City, NY 10005

Attention: Mr. C. P. Goforth

Clark Chemical Corporation
Blue Island Refinery
131 Kedzie Avenue
Blue Island, Illinois

Attention: Mr. R. Bruggink, Director
of Environmental Control

Columbia Nitrogen Corporation
Box 1483
Augusta, Georgia 30903

Attention: Mr. T. F. Champion

Continental Chemical Co.
Park 80 Plaza East
Saddlebrook, NJ 07662

Attention: Mr. J. D. Burns

Cosden Oil & Chemical Co.
Box 1311
Big Spring, Texas 79720

Attention: Mr. W. Gibson

Dart Industries, Inc.
P. O. Box 3157
Terminal Annex
Los Angeles, California 90051

Attention: Mr. R. M. Knight
Pres. Chemical Group

Diamond Plastics
P. O. Box 666
Paramount, California 70723

Attention: Mr. Ben Wadsworth

Diamond Shamrock Chem. Co.
International Division
Union Commerce Building
Cleveland, Ohio 44115

Attention: Mr. W. P. Taylor, Manager
Environ. Control Engineering

Dow Badische Company
Williamsburg, Virginia 23185

Attention: Mr. L. D. Hoblit

Dow Chemical Co. - USA
2020 Building
Abbott Road Center
Midland, Michigan 48640

Attention: Mr. C. E. Otis
Environmental Affairs Div.

E. I. DuPont de Nemours & Co.
Louviers Building
Wilmington, Delaware 19898

Attention: Mr. W. R. Chalker
Marketing Services Dept.

Eastman Chemicals Products, Inc.
Kingsport, Tennessee

Attention: Mr. J. A. Mitchell
Executive Vice President
Manufacturing

El Paso Products Company
Box 3986
Odessa, Texas 79760

Attention: Mr. N. Wright,
Utility and Pollution
Control Department

Enjay Chemical Company
1333 W. Loop South
Houston, Texas

Attention: Mr. T. H. Rhodes

Escambia Chemical Corporation
P. O. Box 467
Pensacola, Florida

Attention: Mr. A. K. McMillan

Ethyl Corporation
P. O. Box 341
Baton Rouge, Louisiana 70821

Attention: Mr. J. H. Huguet

Fibre Industries Inc.
P. O. Box 1749
Greenville, South Carolina 29602

Attention: Mr. Betts

Firestone Plastics Company
Box 699
Pottstown, Pennsylvania 19464

Attention: Mr. C. J. Kleinart

Firestone Synthetic Rubber Co.
381 W. Wilbeth Road
Akron, Ohio 44301

Attention: Mr. R. Pikna

Firestone Plastics Company
Hopewell, Virginia

Attention: Mr. J. Spohn

FMC - Allied Corporation
P. O. Box 8127
South Charleston, W. VA 25303

Attention: Mr. E. E. Sutton

FMC Corporation
1617 J.F.K. Boulevard
Philadelphia, PA

Attention: Mr. R. C. Tower

Foster Grant Co., Inc.
289 Main Street
Ledminster, Mass. 01453

Attention. Mr. W. Mason

G.A.F. Corporation
140 W. 51st Street
New York, NY 10020

Attention: Mr. T. A. Dent, V.P.
of Engineering

General Tire & Rubber Company
1 General Street
Akron, Ohio 44309

Attention: Mr. R. W. Laundrie

Georgia-Pacific Company
900 S.W. 5th Avenue
Portland, Oregan 97204

Attention: Mr. V. Tretter
Sr. Environmental Eng.

Getty Oil Company
Delaware City, Delaware 19706

Attention: Mr. Gordon G. Gaddis

B. F. Goodrich Chemical Co.
6100 Oak Tree Blvd.
Cleveland, Ohio 44131

Attention: Mr. W. Bixby

Goodyear Tire & Rubber Co.
1144 E. Market Street
Akron, Ohio 44316

Attention: Mr. B. C. Johnson, Manager
Environmental Engineering

Great American Chemical Company
650 Water Street
Fitchburg, Mass.

Attention: Dr. Fuhrman

Gulf Oil Corporation
Box 1166
Pittsburgh, Pennsylvania

Attention: Mr. D. L. Matthews
Vice President -
Chemicals Department

Hercules Incorporated
910 Market Street
Wilmington, Delaware

Attention: Dr. R. E. Chaddock

Hooker Chemical Corporation
1515 Summer Street
Stamford, Conn. 06905

Attention: Mr. J. Wilkenfeld

Houston Chemical Company
Box 3785
Beaumont, Texas 77704

Attention: Mr. J. J. McGovern

Hystron Fibers Division
American Hoechst Corporation
P. O. Box 5887
Spartensburg, SC 29301

Attention: Dr. Foerster

Jefferson Chemical Company
Box 53300
Houston, Texas 77052

Attention: Mr. M. A. Herring

Koch Chemical Company
N. Esperson Building
Houston, Texas 77002

Attention: Mr. R. E. Lee

Koppers Company
1528 Koppers Building
Pittsburgh, Pennsylvania 15219

Attention: Mr. D. L. Einon

Marbon Division
Borg-Warner Corporation
Carville, Louisiana 70721

Attention: Mr. J. M. Black

Mobay Chemical Corporation
Parkway West & Rte 22-30
Pittsburgh, Pennsylvania 15205

Attention: Mr. Gene Powers

Mobil Chemical Company
150 E. 42nd Street
New York, NY 10017

Attention: Mr. W. J. Rosenbloom

Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166

Attention: Mr. J. Depp, Director of
Corp. Engineering

National Distillers & Chem. Corp.
U.S. Industrial Chem. Co. Div.
99 Park Avenue
New York, NY 10016

Attention: Mr. J. G. Couch

National Starch & Chem. Co.
1700 W. Front Street
Plainfield, New Jersey 07063

Attention: Mr. Schlass

Northern Petrochemical Company
2350 E. Devon Avenue
Des Plaines, Illinois 60018

Attention: Mr. N. Wacks

Novamont Corporation
Neal Works
P. O. Box 189
Kenova, W. Virginia 25530

Attention: Mr. Fletcher

Olin Corporation
120 Long Ridge Road
Stamford, Conn.

Attention: Mr. C. L. Knowles

Pantasote Corporation
26 Jefferson Street
Passaic, New Jeresy

Attention: Mr. R. Vath

Pennwalt Corporation
Pennwalt Building
3 Parkway
Philadelphia, PA 19102

Attention: Mr. J. McWhirter

Petro-Tex Chemical Corporation
Box 2584
Houston, Texas 77001

Attention: Mr. R. Pruessner

Phillips Petroleum Co.
10 - Phillips Bldg.
Bartlesville, Oklahoma 74004

Attention: Mr. B. F. Ballard

Polymer Corporation, Ltd.
S. Vidal Street
Sarnia, Ontario
Canada

Attention: Mr. J. H. Langstaff
General Manager
Latex Division

Polyvinyl Chemicals Inc.
730 Main Street
Wilmington, Mass. 01887

Attention: Mr. S. Feldman, Director of
Manufacturing - Engineering

PPG Industries Inc.
One-Gateway Center
Pittsburgh, Pennsylvania 15222

Attention: Mr. Z. G. Bell

Reichold Chemicals Inc.
601-707 Woodward Hts. Bldg.
Detroit, Michigan 48220

Attention: Mr. S. Hewett

Rohm & Haas
Independence Mall West
Philadelphia, PA 19105

Attention: Mr. D. W. Kenny

Shell Chemical Co.
2525 Muirworth Drive
Houston, Texas 77025

Attention: Dr. R.L. Maycock
Environ. Eng. Div.

Sinclair-Koppers Chem. Co.
901 Koppers Building
Pittsburgh, Pennsylvania 15219

Attention: Mr. R. C. Smith

Skelly Oil Company
Box 1121
El Dorado, Kansas 67042

Attention: Mr. R. B. Miller

Standard Brands Chem. Industries
Drawer K
Dover, Delaware 19901

Attention: Mr. E. Gienger, Pres.

Stauffer Chemical Co.
Westport, Connecticut

Attention: Mr. E. L. Conant

Stepan Chemical Company
Edens & Winnetka Road
Northfield, Illinois 60093

Attention: Mr. F. Q. Stepan
V.P. - Industrial Chemicals

Tenneco Chemicals Inc.
Park 80 Plaza - West 1
Saddlebrook, NJ 07662

Attention: Mr. W. P. Anderson

Texas - U.S. Chemical Company
Box 667
Port Neches, Texas 77651

Attention: Mr. H. R. Norsworth

Thompson Plastics
Assonet, Mass. 02702

Attention: Mr. S. Cupach

Union Carbide Corporation
Box 8361
South Charleston, W. Virginia 25303

Attention: Mr. G. J. Hanks, Manager
Environ. Protection
Chem. & Plastics Division

Uniroyal Incorporated
Oxford Management &
Research Center
Middlebury, Conn. 06749

Attention: Mr. F. N. Taff

The Upjohn Company
P. O. Box 685
La Porte, Texas

Attention: Mr. E. D. Ike

USS Chemicals Division
U.S. Steel Corporation
Pittsburgh, Pennsylvania 15230

Attention: Mr. Gradon Willard

W. R. Grace & Company
3 Hanover SquarNew York, NY 10004

Attention: Mr. Robt. Goodall

Wright Chemical Corporation
Acme Station
Briegelwood, North Carolina 28456

Attention: Mr. R. B. Catlett

Wyandotte Chemical Corp.
Wyandotte, Michigan 48192

Attention: Mr. John R. Hunter

Vulcan Materials Company
Chemicals Division
P.O. Box 545
Wichita, Kansas 67201

Attention: H.M. Campbell
Vice-President, Production

ENVIRONMENTAL PROTECTION AGENCY

Office of Air Programs
Research Triangle Park, North Carolina 27711

Dear Sir:

The Environmental Protection Agency, Office of Air Programs is engaged in a study of atmospheric emissions from the Petrochemical Industry. The primary purpose of this study is to gather information that will be used to develop New Stationary Source Performance Standards which are defined in Section 111 of the Clean Air Act as amended December 31, 1970 (Public Law 91604). These new source standards will not be set as part of this study but will be based (to a large extent) on the data collected during this study.

A substantial part of the work required for this study will be performed under contract by the Houdry Division of Air Products and Chemicals. Several other companies not yet chosen will assist in the source sampling phase of the work.

Very little has been published on atmospheric emissions from the petrochemical industry. The first part of this study will therefore rank the most important petrochemical processes in their order of importance in regard to atmospheric emissions. The Petrochemical Emissions Survey Questionnaire will be the primary source of data during the first phase. This ranking will be based on the amount and type of emissions from the process, the number of similar processes and the expected growth of the process. A second in-depth phase of the study to document emissions more completely will be based on information obtained through actual stack sampling.

Attached you will find a copy of the petrochemical questionnaire which you are requested to complete and return to the Enviromental Protection Agency within forty-two (42) calender days.

You are required by Section 114 of the Clean Air Act to complete each applicable part of this questionnaire except for question II.4. and II.5. These two questions are concerned with the water and solid waste generated by the process itself not with that generated by the emission control equipment. This information would be of a value to the EPA and your answers will be appreciated.

This questionnaire is to be completed using the information presently available to your company. We are not asking that you perform special non-routine measurements of emissions streams. We are asking for results of measurements that you have made or for estimates when measurements have not been made. Where requested information is not available, please mark sections "not available". Where the requested information is not applicable to the subject process, mark the questionnaire sections "not applicable". A sample questionnaire, filled out for a fictitious process is enclosed for your guidance.

It is the opinion of this office that for most processes it should be possible to answer all survey questions without revealing any confidential information or trade secrets. However, if you believe that any of the information that we request would reveal a trade secret if divulged you should clearly identify such information on the completed questionnaire. Submit, with the completed questionnaire, a written justification explaining the reason for confidential status for each item including any supportive data or legal authority. Forward a duplicate of your claim and supporting material, without the questionnaire data, to our counsel, Mr. Robert Baum, Assistant General Counsel, Air Quality and Radiation Division, Environmental Protection Agency, Room 17B41, 5600 Fishers Lane, Rockville, Maryland 20852. Emission data cannot be considered confidential.

Final authority for determining the status of the information resides with the Enviromental Protection Agency. A reply describing the decision reached will be made as soon as possible after receipt of the claim and supporting information. During the period before the final determination this office will honor any request to treat the questionnaire information as confidential.

Information declared to be a trade secret is subject to protection from being published, divulged, disclosed or made known in any manner or to any extent by Section 1905 of Title 18 of the United States Code. The disclosure of such information, except as authorized by law, shall result in a fine of not more than $1,000 or imprisonment of not more than one year, or both; and shall result in removal of the individual from his office or employment.

Although it should be noted that Section 114, Subsection C of the Clean Air Act allows such information to be disclosed "to other officers, employees, or authorized representatives of the United States concerned with carrying out the Act or when relevant in any proceeding under this Act," no confidential information will be revealed to any private concern employed by the Environmental Protection Agency to assist in this study.

The handling and storage of information for which the determination is pending or information which has been determined to be of a confidential nature is carefully controlled. Preliminary control procedures require that the material be labeled confidential and stored in a locked file.

The complete form should be mailed to:

Mr. Leslie B. Evans
Environmental Protection Agency
Office of Air Programs
Applied Technology Division
Research Triangle Park, NC 27711

It is possible that additional copies of this questionnaire which will request information covering other petrochemical processes or other plants using the same process and operated by your organization will be sent to you in the course of this study. Clarification of items contained in the questionnaire may be obtained from Mr. Evans by telephone at 919/688-8146. Thank your for your help in this matter.

Sincerely,

Leslie B. Evans

Leslie B. Evans
Industrial Studies Branch

Petrochemical Questionnaire

Instructions

I. **Capacity.** Describe capacity of process by providing the following:

1. Process capacity. Give capacity in units per year and units per hour. An "actual" capacity is preferred but "published" or "name plate" capacity will be satisfactory if such capacity is reasonably correct. Do not give production.

2. Seasonal variation. Describe any significant seasonal variations in production.

   As example an ammonia plant might produce more during spring and winter quarters:

quarter	Jan-Mar	April-June	July-Sept	Oct-Dec	Year Total
%	40	20	10	30	100%

II. Process. Describe the process used to manufacture the subject chemical by providing the following:

1. Process name. If the process has a common name or description, give this. If any portion of the process (e.g., product recovery method) has a common name, give this.

2. Block Diagram. Provide a block diagram of the process showing the major process steps and stream flows.

   (a) Show on block diagram all streams described below. Identify each required stream by letter. (A,B,C, etc.) In general the streams that must be identified are (1) the gaseous emissions streams before and after any control device and (2) the gaseous or liquid streams which, after leaving the process site, produce gaseous emissions during further processing or combustion.

   (1) Any gaseous waste streams before and after any pollution device should be shown and identified.

   (ii) Streams from rupture disks or pressure relief valves which protect equipment from operating upsets but discharges less than once every year need not be shown.

   (iii) Emissions from pressure relief systems that normally discharge during power failures or other emergencies should be shown, identified by letter and labeled "emergency".

(iv) Emissions from fueled heaters such as "heat transfer medium" heaters, steam generators, or cracking furnaces need not be shown if they are fueled completely by fuels listed in Question VII and are not used to incinerate by-products or off gases.

(v) Emissions from Claus units associated with process need not be shown. Stream to Claus unit should be shown and identified with letter.

(vi) Emissions from a central power plant (or steam plant) which burns a liquid fuel produced as a by-product of this process need not be shown. Such liquid fuel should be shown and identified by letter.

(vii) Emissions from a central power plant (or steam plant) which burns a gaseous fuel produced as a by-product of this process need not be shown. Such gaseous fuel should be shown and identified by letter.

(b) Show all gaseous emission control devices. Identify each control device on the block diagram by a three digit number (101, 102, 103, etc.)

(c) Show all stacks or vents that vent streams listed in (a) and (b) above. It a stack to vent discharges emissions from more than one source, label this stack or vent with a letter in sequence started in II.2.a. (D,E,F, etc.) If a stack or vent discharges emissions from only one source label the stack with the same letter as the emission stream.

3. Raw material and product. Give approximate chemical composition and approximate amount (on yearly basis and at capacity given in I.1) of all raw-materials, products and by-products. If composition or amounts vary, give ranges. Composition may be given in commonly accepted terms when a chemical analysis would be inappropriate. The description "light straight-run naphtha" would be adequate.

4. Waste water. Is there a waste water discharge from this process which is (eventually) discharged to a receiving body of water? Is this waste water treated by you or by others? Give the approximate volume and indicate whether this is measured or estimated.

5. Waste solids. Is there a waste solids discharge from this process? How is it disposed of? Give the approximate daily total of waste solids and indicate if this is measured or estimated.

III. Emissions (composition and flow): For each stream requested in II.2.a. and shown on the block diagram by letter provide the following: (Use separate sheets for each identified location - 6 copies are provided). All of the questions will not be applicable for each stream.

As an example, question 10, odor problem, applies only to streams which are emitted to the atmosphere.

1. Chemical composition and flow. Give composition as completely as possible from information you have available. Do not omit trace constituents if they are known. If anything (e.g. fuel) is added upstream of any emission control devices, give the chemical composition and flow prior to the addition, and give the quantity and composition of the added material. If liquids or solids are present (in gas stream) provide the composition and amount of these also. Give flow volume (SCFM), temperature (F°) and pressure (psig or inches H_2O).

2. Variation in chemical composition and flow. If average stream composition or flow varies significantly over some period of time during normal or abnormal operation, discuss this variation and its frequency. Relate this to the average and range of composition given in III.1.

   As examples:

   "During start-up (once a month) the benzene is about 12% by volume for one hour" or "the benzene can be expected to go from 5% to 9% by volume during life of catalyst, the 'average' figure given is about average over the catalyst life" or "power failures occur about once each winter causing stream A to increase from 0 to (initially) 50,000 lbs/hr., and about 8,000 lbs is vented over a 15 minute period."

3. Production rate during sampling. If stream composition and volume flow rates given in answer to questions III.1. and III.2. were measured at a plant production rate different than the capacity of the plant given in I.1. give the rate at which the measurements were made.

   As example:

   Figures given for this stream (A) were made when plant was operating at 90% of capacity given in I.1.

4. Methods used to determine composition and flow. Is information from material balance, from sample and analysis, or other? Describe briefly.

5. Sampling procedure. If samples have been taken, give summary description of sampling procedure or give reference if described in open literature.

6. Analytical procedure. If samples have been taken, give summary description of analytical procedure or give reference if described in open literature.

7. Sampling frequency. How often is the stream sampled?

   As Examples:

   "continuous monitor" or "twice a shift for last 18 months" or "once in the fall of 1943".

8. Confidence level. Give some idea how confident you are in regard to compositions in III.1.

   As examples:

   "probably correct ± 20%" or "slightly better than wild guess".

9. Ease of sampling. How difficult is it to sample this stream?

   As examples:

   "sample line runs into control room" or "sample port provided but accessible only with 20-ft. ladder."

10. Odor problem. Is the odor of this emission detectable at ground level on the plant property or off the plant property? If odors carry beyond the plant property are they detectable frequently or infrequently? Have you received a community odor complaint traceable to this source in the past year? Has the odorous material been chemically identified? What is it?

IV. Emission control device. Supply the following information for each control device shown on the block diagram. (Use separate sheets for each - 3 copies are provided).

1. Engineering description. Give brief description and process sketch of the control device. Attach print or other description if you prefer. Show utilities used, steam produced, product recovered, etc. Give manufacturer, model number and size (if applicable). Give complete (applicable) operating conditions, i.e. flows, temperatures, pressure drops, etc.

2. Capital cost of emission control system.

   (a) Give capital cost for the emission control device as it is described in IV.1. above; i.e., if equipment has been modified or rebuilt give your best estimate of capital cost of equipment now in service. For the total installed cost give the approximate breakdown by year in which cost was incurred.

   As example:

Major equipment cost	$155,000
Total installed cost	$250,000

Year	Cost
1963	$160,000
1964	40,000
1971	50,000
	$250,000

   (b) On the check list given mark whether the items listed are included in total cost as given above. Give one sentence explanation when required but do not give dollar amounts.

   (c) Was outside engineering contractor used and was cost included in capital cost?

   (d) Was in-house engineering used and was cost included in capital cost?

   (e) Was emission control equipment installed when plant was built?

3. Operating cost of emission control system. Give the best estimate of cost of operating emission control system in dollars per year with process operated at capacity given in I.1. Other disposal (g) would include, as example, the cost of incinerating a by-product stream which has no value.

V. Stack or vent description. Each stack or vent should have been identified by letter on the block diagram. Provide the requested information for each stack. Stack flow, V.4. should be entered only when it is not possible to calculate this number by adding gas flows given in III.1.

An example would be when an off gas from the process is discharged into a power plant stack.

VI. Tankage. Give information requested for all tankage larger than 20,000 gallons associated with the process and normally held at atmospheric pressure (include raw material, process, product and by-product tankage). Method of vapor conservation (3.) might include, as examples:

"none, tank vents to air"
"floating roof"
"vapor recovery by compression and absorption".

VII. Fuels. If fuels are used in the process give the amount used on a yearly basis at capacity given in I.1. Do not include fuel used in steam power plants. Give sulfur content. Identify each fuel as to its source (natural gas pipeline, process waste stream, Pennsylvania soft coal). Is the fuel used only as a heat source (as with in-line burner)?

VIII. Other emissions. If there is a loss of a volatile material from the plants through system leaks, valve stems, safety valves, pump seals, line blowing, etc., this loss is an emission. In a large complex high pressure process this loss may be several percent of the product. Has this loss been determined by material balance or other method? What is it? Give best estimate.

IX. Future plans. Describe, in a paragraph, your program for the future installation of air pollution control equipment for this unit or for future improvements in the process which will reduce emissions.

OMB Approval Number 158 S 72019

This example questionnaire has been completed for a fictitious company and process.

Example Questionnaire

Air Pollution Control Engineering and Cost Study of the Petrochemical Industry

Please read instructions before completing questionnaire.

Subject chemical: Pyrrole

Principal by-products: Pyrrolidone

Parent corporation name: Orivne Petrochemical Co.

Subsidiary name: Noissime Division

Mailing address: P.O. Box 1234
Rianaelc, North Carolina, 27700

Plant name: Rianaelc Plant

Physical location: 30 miles N.W. Durham, North Carolina

(include county and
air quaility control
region) Orange County; Eastern Piedmont Intrastate (Region IV)

Person EPA should contact regarding information supplied in this questionnaire

Name: John Doe

Title: Supervisor of Process Development

Mailing address: Noissime Division of O.P.C.
P.O. Box 1234
Rianaelc, North Carolina, 27700

Telephone number: 919 XXX XXXX

Date questionnaire completed: May 30, 1972

I. Capacity.

1. Process capacity. (not production)

80,000,000 lbs. per year

10,000 lbs. per hour

2. Seasonal variation. (of production)

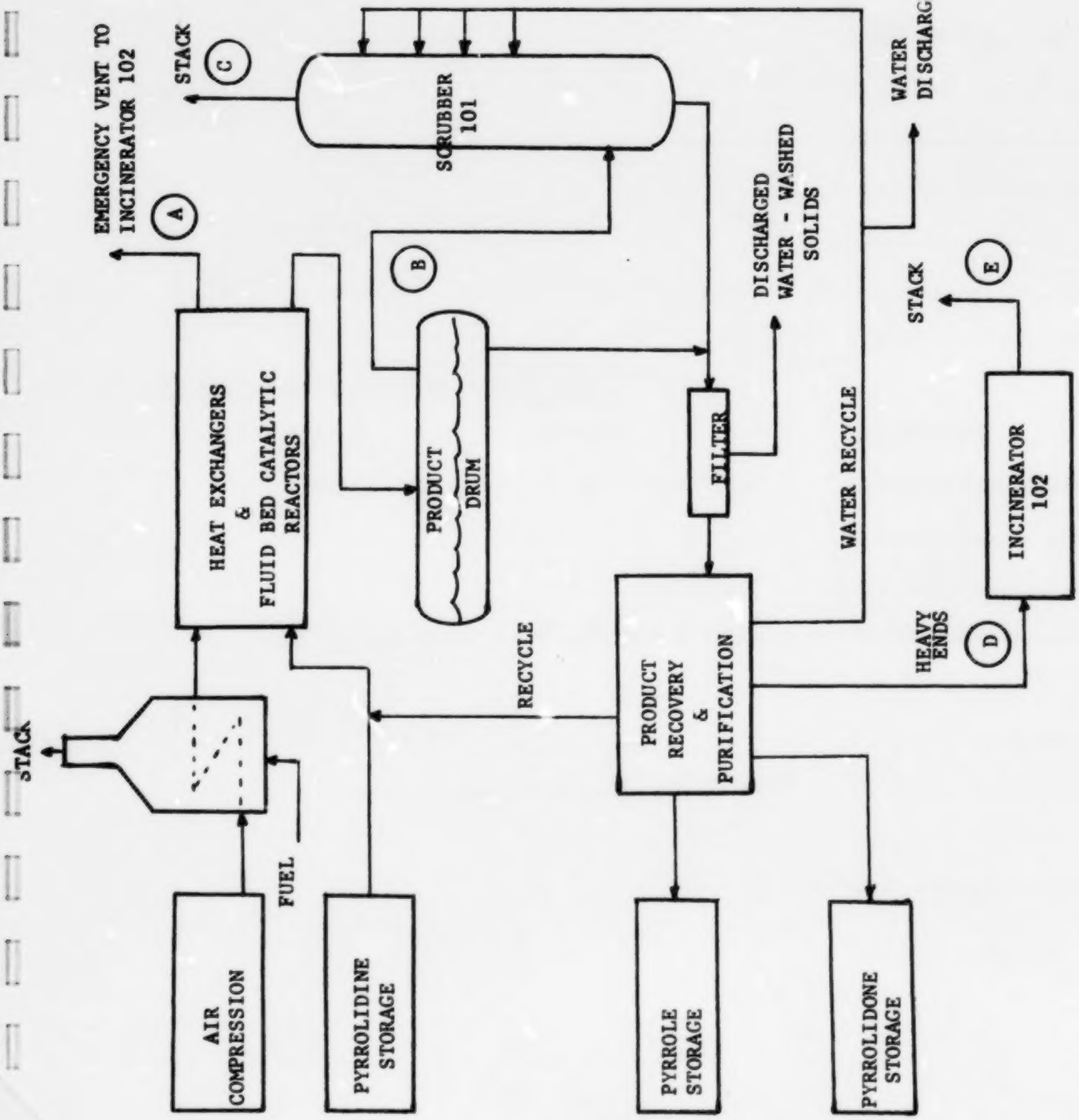
quarter	1	2	3	4	year total
%	30	20	20	30	100%

II. Process.

1. Process name.

Reivrep - Process (oxidative dehydrogenation of pyrrolidine)

2. Block diagram.


EMERGENCY VENT TO INCINERATOR 102
A
STACK
C
SCRUBBER 101
WATER DISCHARGE
B
DISCHARGED WATER - WASHED SOLIDS
STACK
E
HEAT EXCHANGERS & FLUID BED CATALYTIC REACTORS
PRODUCT DRUM
FILTER
WATER RECYCLE
INCINERATOR 102
RECYCLE
HEAVY ENDS
D
STACK
PRODUCT RECOVERY & PURIFICATION
FUEL
AIR COMPRESSION
PYRROLIDINE STORAGE
PYRROLE STORAGE
PYRROLIDONE STORAGE

II. Process. (Continued)

3. Raw materials and products

Raw materials

Name	Quantity	Composition
Pyrrolidine	130,000,000 lbs/yr.	pyrrolidine 98%
		other amines 2%

Product and by-products

Name	Quantity	Composition
Pyrrole	80,000,000 lbs/yr.	pyrrole 99.5%
Pyrrolidone	20,000,000 lbs/yr.	pyrrolidone 99.5%

II. Process. (Continued)

4. Waste water.

750 gal/hr. treated by us, measured in treatment unit.

5. Waste solids.

200 lbs/hr. catalyst dust from filter. Estimated average quantity hauled away by solids waste disposal contractor.

III. 1. Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter ___A___.

1. Flow ___?___ Temperature ___?___ Pressure ______.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid		

Depending upon cause of emergency, emissions could range from contaminated feed to contaminated product. Upset durations seldom exceed 15 minutes during which time incinerator operation would be modified. For initial 1-2 minutes after upset pollutants might leave incinerator stack. Following that, stack gases will be nearly 100% CO_2, H_2O & N_2. On average, such upsets occur two or three times per year. Particulates are possible, depending upon cause of upset. One such upset occurred in 1969.

* Particulate matter should be described as fully as possible. ______

III. Continued For stream flow shown on block diagram by letter A.

2. Composition variation.

See III-1

3. Production rate during sampling.

Never Sampled

4. Method used to determine composition and flow.

Not applicable

III. Continued For stream flow shown on block diagram by letter A.

5. Sampling procedure.

   Not Applicable

6. Analytical procedure.

   Not Applicable

7. Sampling frequency.

   Never

III. Continued For stream flow shown on block diagram by letter A.

8. Confidence level.

Not Applicable

9. Ease of sampling.

Impossible

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/no Off the plant property? Yes/no If odors carry beyond the plant property are they detectable infrequently? Yes/no Frequently? Yes/no Have you received a community odor complaint traceable to this source in the past year? Yes/no Has the odorous material been chemically identified? Yes/no What is it?____________________

Not Applicable

III.1. Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter B .

1. Flow 10,000 SCFM Temperature 110°F Pressure 25 PSIG .

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	150 lbs./hour	100-200 lbs./hour
Nitrogen	N_2	Gas	83.8 Vol. %	80-85%
Oxygen	O_2	Gas	1.4 "	1-2%
Carbon Monoxide	CO	Gas	4.1 "	3-5%
Carbon Dioxide	CO_2	Gas	1.4 "	1-2%
Hydrogen	H_2	Gas	2.1 "	2-2.5%
Water	H_2O	Vapor	7.1 "	6.5-7.5%
Various Amines	**	Vapor	0.1 "	0.05-0.2%
Nitrogen Oxides	NO_x	Gas	300 VPPM	200-500 VPPM

* Particulate matter should be described as fully as possible. Catalyst Dust (composition is proprietary) contains cobalt and chromium on alumina base. 100% less than 15 microns; 60% less than 10 microns; 20% less than 5 microns; 5% less than 1 micron.

** Composition unknown - mixture of feed, products and other amines.

III. Continued For stream flow shown on block diagram by letter B.

2. Composition variation.

During 2nd and 3rd quarter when plant is operated below capacity, nitrogen is at high end of range and all other materials near low end. During start-up or plant upset (average about 50 hours/year) nitrogen is near low end of range and all other materials near high end.

3. Production rate during sampling.

Average composition based on rated capacity.

4. Method used to determine composition and flow.

Engineering calculation and plant material balance (flow). Composition calculated on basis of stream "C" analysis and estimated amine losses prior to installation of scrubber.

III. Continued For stream flow shown on block diagram by letter B .

5. Sampling procedure.

Never sampled.

6. Analytical procedure.

Never Analyzed.

7. Sampling frequency.

See (5) above.

III. Continued For stream flow shown on block diagram by letter B.

8. Confidence level.

± 10%

9. Ease of sampling.

No sample taps are available, but one could be easily installed in readily accessible location. However, it would not be 8 pipe diameters from a disturbance.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/no Off the plant property? Yes/no If odors carry beyond the plant property are they detectable infrequently? Yes/no Frequently? Yes/no Have you received a community odor complaint traceable to this source in the past year? Yes/no Has the odorous material been chemically identified? Yes/no What is it?

No applicable - this stream is no longer emitted to the atmosphere.

III. 1. Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter C.

1. Flow 10,000SCFM Temperature 100°F Pressure 0 PSIG.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	10 lbs./hour	5-20 lbs./hour
Nitrogen	N_2	Gas	83.9 Vol. %	80-85%
Oxygen	O_2	Gas	1.4 "	1-2%
Carbon Monoxide	CO	Gas	4.1 "	3-5%
Carbon Dioxide	CO_2	Gas	1.4 "	1-2%
Hydrogen	H_2	Gas	2.1 "	2-2.5%
Water	H_2O	Vapor	7.1 "	6.5-7.5%
Various Amine	**	Vapor	50 YPPMV	30-100 PPMV
Nitrogen Oxides	NO_x	Gas	300 YPPMV	200-500 PPMV

* Particulate matter should be described as fully as possible. See "B". Size distribution 100% less than 5 microns; 60% less than 1 micron.

** See "B".

III. Continued For stream flow shown on block diagram by letter C .

2. Composition variation.

See "B"

3. Production rate during sampling.

See "B"

4. Method used to determine composition and flow.

See "B" for flow. Specific analysis methods are given in III-6(C)

III. Continued For stream flow shown on block diagram by letter C.

5. Sampling procedure.

a. Particulates and moisture collected in sampling train as detailed in Federal Register, Dec. 23, 1971 (Method 5).

b. NO_x sampled by EPA Method 7.

c. Other constituents collected using grab sampling procedures for collection of gas. Sample size 10 liters in stainless steel tank.

6. Analytical procedure.

a. Particulates and moisture determined gravimetrically as detailed in Federal Register, Dec. 23, 1971. (Method 5)

b. NO_x determined by EPA method 7.

c. Hydrogen, oxygen, and nitrogen determined by mass spectrometer analysis at local university.

Amine, CO and CO_2 determined by infra-red analysis.

7. Sampling frequency.

Once, - one month after scrubber was put on stream.

III. Continued For stream flow shown on block diagram by letter C.

8. Confidence level.

Oxygen, CO_2, CO and H may be ± 10%.

Nitrogen would be better than this, perhaps ± 5%

Amines are near limit of detection - ± 50%.

9. Ease of sampling.

Difficult - only sample tap is six feet above top of scrubber tower - approximately 65 feet in air - reached by caged ladders.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? [✓ Yes]/no Off the plant property? [✓ Yes]/no If odors carry beyond the plant property are they detectable infrequently? [✓ Yes]/no Frequently? Yes/[✓ no] Have you received a community odor complaint traceable to this source in the past year? Yes/[✓ no] Has the odorous material been chemically identified? [✓ Yes]/no What is it? Amine compounds.

III.1.Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter D.

1. Flow 300 GPH Temperature 300°F Pressure 10 PSIG.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	Trace	
Heavy Amines	$(CH_x)_yNH_z$	Liquid	100%	

* Particulate matter should be described as fully as possible. Very fine catalyst dust - never sampled or analyzed - estimated to be 1-5 lbs./hour.

III. Continued For stream flow shown on block diagram by letter D.

2. Composition variation.

Not applicable - unknown - never analyzed.

3. Production rate during sampling.

See "B"

4. Method used to determine composition and flow.

Rotameter in liquid line for flow. Composition unknown.

III. Continued For stream flow shown on block diagram by letter D.

5. Sampling procedure.

Not applicable.

6. Analytical procedure.

Not applicable.

7. Sampling frequency.

Not applicable.

III. Continued For stream flow shown on block diagram by letter D.

8. Confidence level.

Not applicable.

9. Ease of sampling.

Liquid drain line is available at ground level. Could be used for sample tap.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/no Off the plant property? Yes/no If odors carry beyond the plant property are they detectable infrequently? Yes/no Frequently? Yes/no Have you received a community odor complaint traceable to this source in the past year? Yes/no Has the odorous material been chemically identified? Yes/no What is it?____________________

Not applicable - not an emitted stream.

III. 1 Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter ___E___.

1. Flow 10,000SCFM Temperature 450°F Pressure 0 PSIG.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	Trace	
Nitrogen	N_2	Gas	77.0 Vol. %	76.5-77.5%
Oxygen	O_2	Gas	9.2 Vol. %	9-9.5%
Carbon Dioxide	CO_2	Gas	6.4 Vol. %	6-7%
Water	H_2O	Vapor	7.4 Vol. %	7-8%
Nitrogen Oxides	NO_x	Gas	150 VPPM	100-300 VPPM

* Particulate matter should be described as fully as possible. See "D"

III. Continued For stream flow shown on block diagram by letter E.

2. Composition variation.

Random variation depending on many variables such as production rate, ambient air temperature and humidity, catalyst age, etc., all within limits shown.

3. Production rate during sampling.

See "B"

4. Method used to determine composition and flow.

Calculation based on incinerator vendor's specifications, guarantees and laboratory tests.

III. Continued For stream flow shown on block diagram by letter ____E____.

5. Sampling procedure.

Never sampled.

6. Analytical procedure.

Never analyzed

7. Sampling frequency.

See (5) above

III. Continued For stream flow shown on block diagram by letter E.

8. Confidence level.

± 10%

9. Ease of sampling.

No sample tap, very hot stream, no access ladders, minimal insulation.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/[✓ no] Off the plant property? [✓ Yes]/no If odors carry beyond the plant property are they detectable infrequently?* [✓ Yes]/no Frequently? Yes/[✓ no] Have you received a community odor complaint traceable to this source in the past year? Yes/[✓ no] Has the odorous material been chemically identified? [✓ Yes]/no What is it? Amines

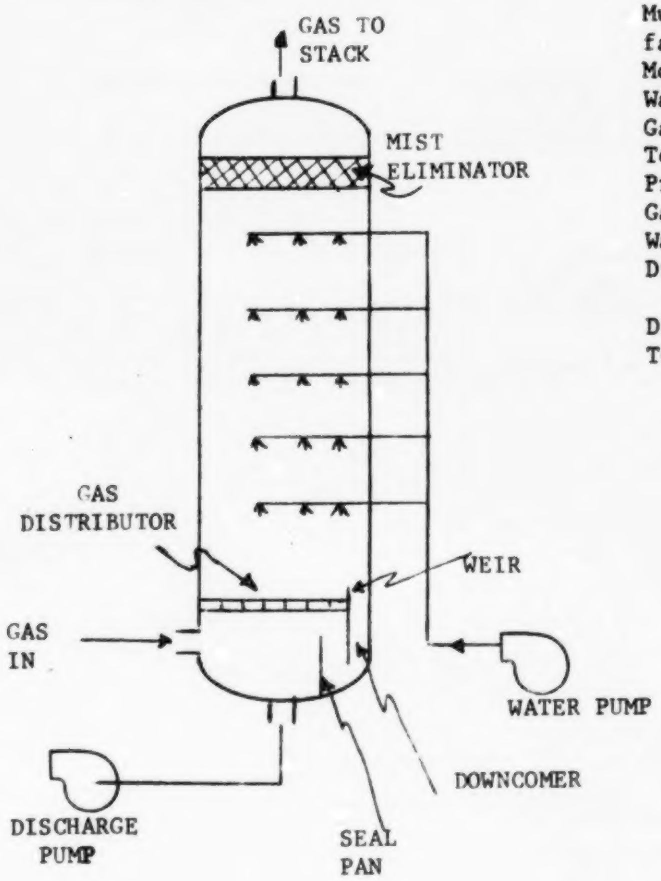
* Only during start-up or upset of the incinerator and then only if atmospheric conditions are favorable for ground level detection.

3 copies provided
this section.

IV. Emission control device

For device shown on block diagram by number 101.

1. Engineering description.


GAS TO STACK
MIST ELIMINATOR
GAS DISTRIBUTOR
WEIR
GAS IN
WATER PUMP
DOWNCOMER
DISCHARGE PUMP
SEAL PAN

Multi-nozzle spray tower manufactured by Rebburcs Corp.
Model No. 10,000-W
Water rate: 100 GPM
Gas rate: 10,000 SCFM
Temperature: 100°F.
Pressure: Atmospheric
Gas AP: 8 in, H_2O
Water Pump Head: 150 Ft.
Discharge Pump Head: 100 Ft.

Diameter of Tower: 6 Ft.
T-T Length: 60 Ft.

Utilities:

35 HP for Pumps

10,000,000 BTU/Hr. Additional steam in product recovery section.

1500 GPM Additional cooling water circulation in product recovery section.

IV. Continued For device shown on block diagram by number 101 .

2. Capital cost of emission control system.

(a) Capital cost

Major equipment cost $ 160,000

Total installed cost $ 350,000

Year	Cost
1968	$350,000

IV. Continued For device shown on block diagram by number 101.

(b) Check list. Mark whether items listed are included in total cost included in IV.2.a. Do not give dollar value -

Yes	No	Cost	Explanation
X		Site development	Additional foundation required for scrubber.
	X	Buildings	
	X	Laboratory equipment	
X		Stack	
X		Rigging etc.	
X		Piping	
X		Insulation	
X		Instruments	
	X	Instrument panels	
X		Electrical	
	X	Facilities outside battery limits*	
	X	Storage tanks, spheres drums, bins, silos	
	X	Catalysts	
	X	Spare parts and non-installed parts	

*Such as - process pipe lines such as steam, condensate, water, gas, fuel, air, fire, instrument and electric lines.

IV. Continued For device shown on block diagram by number 101 .

Yes	No	
X		Was outside engineering contractor used?
X		Was cost included in capital cost?
X		Was in-house engineering used?
	X	Was cost included in capital cost?
	X	Was emission control equipment installed and constructed at the time plant (process) was constructed?

3. Operating costs of control system.

Give 1972 dollar values per year at capacity given in I.1.

(a)	Utilities	$ 68,000
(b)	Chemicals *	10,000
(c)	Labor (No Additional Operators)	-
(d)	Maintenance (labor & materials)	14,000
(e)	Water treatment (cost of treating any waste water produced by this control system) **	-
(f)	Solids remmoval (cost of removing any waste solids produced by this control system)	20,000
(g)	Other disposal	-
(h)	By-product or product recovery CREDIT	(89,000)
	Total operating costs	$ 23,000

* Additional cooling water treatment included in utility costs - this cost is for corrosion inhibition in scrubber.

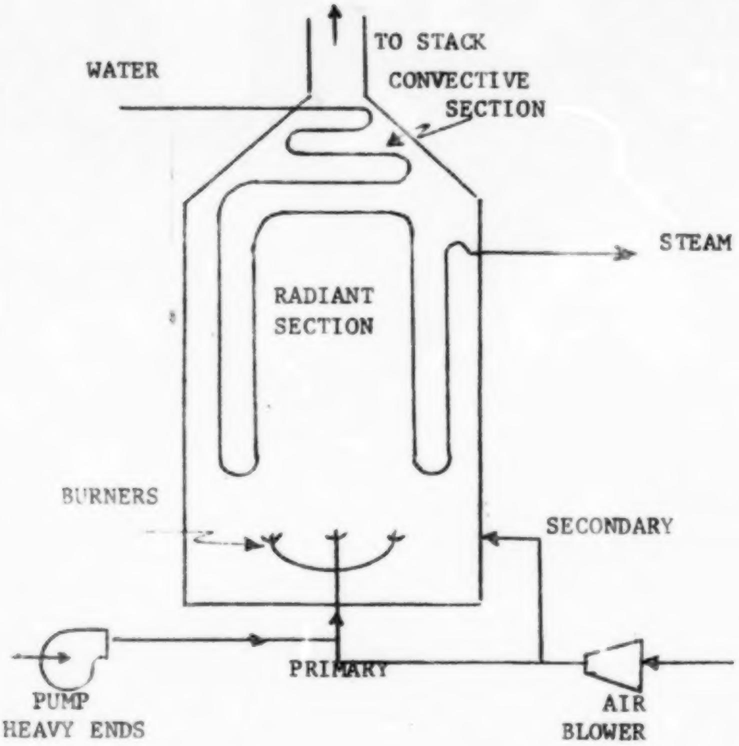
** Water waste is produced by process. It is treated at cost of $30,000/year. This treatment was required before scrubber was installed.

3 copies provided
this section.

IV. Emission control device

For device shown on block diagram by number 102.

1. Engineering description.


TO STACK
WATER
CONVECTIVE SECTION
STEAM
RADIANT SECTION
BURNERS
SECONDARY
PRIMARY
PUMP HEAVY ENDS
AIR BLOWER

Steam Generator/Waste Incinerator

Manufactured by: Xoberif Corp.
Model No.: 40-H
Heavy Ends Rate: 300 GPH
Air Rate: 9,500 SCFM
Steam Rate: 20,000 lbs./hour
Vessel Diameter: 15 Ft.
Height: 40 Ft.
Tube Diameter: 3 in. nominal
Tube Length: (Material)
  Convective (mild steel): 6,000 Ft.
  Radiant (304 stainless): 2,000 Ft.

Utilities:

Heavy Ends Pump: 20 HP

Blower: 100 HP

IV. Continued For device shown on block diagram by number 102.

2. Capital cost of emission control system.

(a) Capital cost

Major equipment cost $ 350,000

Total installed cost $ 1,000,000

Year	Cost
1960	$1,000,000

IV. Continued For device shown on block diagram by number 102.

(b) Check list. Mark whether items listed are included in total cost included in IV.2.a. Do not give dollar value -

Yes	No	Cost	Explanation
X		Site development	Cost prorated from total plant site costs.
	X	Buildings	
	X	Laboratory equipment	
X		Stack	
X		Rigging etc.	
X		Piping	
X		Insulation	
X		Instruments	
X		Instrument panels	
X		Electrical	
	X	Facilities outside battery limits*	
	X	Storage tanks, spheres drums, bins, silos	
	X	Catalysts	
	X	Spare parts and non-installed parts	

*Such as - process pipe lines such as steam, condensate, water, gas, fuel, air, fire, instrument and electric lines.

IV. Continued For device shown on block diagram by number 102 .

Yes	No	
X		Was outside engineering contractor used?
X		Was cost included in capital cost?
	X	Was in-house engineering used?
X		Was cost included in capital cost?
X		Was emission control equipment installed and constructed at the time plant (process) was constructed?

3. Operating costs of control system.

Give 1972 dollar values per year at capacity given in I.1.

(a)	Utilities	$ 5,000
(b)	Chemicals	-
(c)	Labor (½ man per shift - excludes supervision & overhead)	7,000
(d)	Maintenance (labor & materials)	40,000
(e)	Water treatment (cost of treating any waste water produced by this control system)	-
(f)	Solids remmoval (cost of removing any waste solids produced by this control system)	-
(g)	Other disposal	-
(h)	By-product or product recovery CREDIT- STEAM	($100,000)
	Total operating **credit**	$ 48,000

V. Stack or vent description.

For stack or vent shown on block diagram by letter C.

1. Stack height 100 ft
2. Stack diameter 2 ft
3. Gas temperature stack exit 100 °F
4. Stack flow * SCFM(70°F & 1 Atm.)

For stack or vent shown on block diagram by letter E.

1. Stack height 60 Ft.
2. Stack diameter 3 Ft.
3. Gas temperature stack exit 450°F
4. Stack flow * ______

For stack or vent shown on block diagram by letter ______.

1. Stack height ______
2. Stack diameter ______
3. Gas temperature stack exit ______
4. Stack flow * ______

For stack or vent shown on block diagram by letter ______.

1. Stack height ______
2. Stack diameter ______
3. Gas temperature stack exit ______
4. Stack flow * ______

* See instructions

VI. Tankage.

No. of tanks	composition	temp.	capacity (each)	approximate turnovers per year	method of vapor conservation
3	Pyrrolidine $(CH_2)_4NH$	Ambient	100,000 gal.(ea)	50	None, vents to air
4	Pyrrole $(CH)_4NH$	Ambient	100,000 gal.(ea)	25	"
1	Pyrrolidone $(CH)_2CH_2CONH$	Ambient	100,000 gal.(ea)	25	"

VII. Fuels.

800,000 gal./year fuel oil for fired air heater 3% sulfur.

VIII. Other emissions.

No other known emissions although minor leakages probably occur.

Engineering estimate of average losses is 0.01% of throughput or 13,000 lbs./year of amines.

IX. Future plans.

1. Current research on heavy amine stream indicates further processing will produce a marketable product - if so, incinerator will be shut down.
2. We are currently negotiating a long term contract to purchase 1% sulfur fuel oil from the Flused Oil Company.

APPENDIX III

FINAL QUESTIONNAIRE SUMMARY

Chemical	Number of Questionnaires used as Basis for Report
Acetaldehyde via Ethylene	1
via Ethanol	1
Acetic Acid via Methanol	2
via Butane	1
via Acetaldehyde	1
Acetic Anhydride	2
Acrylonitrile	4
Adipic Acid	4
Adiponitrile via Butadiene	1
via Adipic Acid	2
Carbon Black	7
Carbon Disulfide	4
Cyclohexanone	7
Dimethyl Terephthalate (+TPA)	6
Ethylene	13
Ethylene Dichloride via Oxychlorination	10
via Direct Chlorination	3
Ethylene Oxide	7
Formaldehyde via Silver Catalyst	12
via Iron Oxide Catalyst	6
Glycerol	2
Hydrogen Cyanide	1
Isocyanates	10
Maleic Anhydride	7
Nylon 6	4
Nylon 6,6	3
Oxo Process	6
Phenol	8
Phthalic Anhydride via o-xylene	5
via naphthalene	3
Polyethylene (High Density)	5
Polyethylene (Low Density)	7
Polypropylene	7
Polystyrene	4
Polyvinyl Chloride	8
Styrene	7
Styrene - Butadiene Rubber	6
Vinyl Acetate via Acetylene	3
via Ethylene	1
Vinyl Chloride	8

INTRODUCTION TO APPENDIX IV AND V

The following discussions describe techniques that were developed for the single purpose of providing a portion of the guidance required in the selection of processes for in-depth study. It is believed that the underlying concepts of these techniques are sound. However, use of them without substantial further refinement is discouraged because the data base for their specifics is not sufficiently accurate for wide application. The subjects covered in the Appendix IV discussion are:

1. Prediction of numbers of new plants.
2. Prediction of emissions from the new plants on a weighted (significance) basis.

The subject covered in the Appendix V discussion is:

Calculation of pollution control device efficiency on a variety of bases, including a weighted (significance) basis.

It should be noted that the weighting factors used are arbitrary. Hence, if any reader of this report wishes to determine the effect of different weighing factors, the calculation technique permits changes in these, at the reader's discretion.

APPENDIX IV

Number of New Plants by 1980

Attached Table 1 illustrates the format for this calculation. Briefly, the procedure is as follows:

1. For each petrochemical that is to be evaluated, estimate what amount of today's production capacity is likely to be on-stream in 1980. This will be done by subtracting plants having marginal economics due either to their size or to the employment of an out-of-date process.

2. Estimate the 1980 demand for the chemical and assume a 1980 installed capacity that will be required in order to satisfy this demand.

3. Estimate the portion of the excess of the 1980 required capacity over today's remaining capacity that will be made up by installation of each process that is being evaluated.

4. Estimate an economic plant or unit size on the basis of today's technology.

5. Divide the total required new capacity for each process by the economic plant size to obtain the number of new units.

In order to illustrate the procedure, data have been incorporated into Table I, for the three processes for producing carbon black, namely the furnace process, the relatively non-polluting thermal process, and the non-growth channel process.

Table 1. Number of New Plants by 1980

Chemical	Process	Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
Carbon Black	Furnace	4,000	0	4,000	4,500	5,000	1,000	90	11 - 12
	Channel	100	0	100	100	100	0	30	0
	Thermal	200	0	200	400	500	300	150	2

Notes: 1. Capacity units all in MM lbs./year.

2. 1980 demand based on studies prepared for EPA by Processes Research, Inc. and MSA Research Corporation.

Increased Emissions (Weighted) by 1980

Attached Table 2 illustrates the format for this calculation. However, more important than format is a proposal for a weighting basis. There is a wide divergence of opinion on which pollutants are more noxious and even when agreement can be reached on an order of noxiousness, disagreements remain as to relative magnitudes for tolerance factors. In general pollutants from the petrochemical industry can be broken down into categories of hydrogen sulfide, hydrocarbons, particulates, carbon monoxide, and oxides of sulfur and nitrogen. Of course, two of these can be further broken down; hydrocarbons into paraffins, olefins, chlorinated hydrocarbons, nitrogen or sulfur bearing hydrocarbons, etc. and particulates into ash, catalyst, finely divided end products, etc. It is felt that no useful end is served by creating a large number of sub-groupings because it will merely compound the problem of assigning a weighting factor. Therefore, it is proposed to classify all pollutants into one of five of the six categories with hydrogen sulfide included with hydrocarbons.

There appears to be general agreement among the experts that carbon monoxide is the least noxious of the five and that NO_x is somewhat more noxious than SO_x. However, there are widely divergent opinions concerning hydrocarbons and particulates - probably due to the fact that these are both widely divergent categories. In recent years, at least two authors have attempted to assign tolerance factors to these five categories. Babcock (1), based his on the proposed 1969 California standards for one hour ambient air conditions with his own standard used for hydrocarbons.

On the other hand, Walther (2), based his ranking on both primary and secondary standards for a 24-hour period. Both authors found it necessary to extrapolate some of the basic standards to the chosen time period. Their rankings, on an effect factor basis with carbon monoxide arbitrarily used as a reference are as follows:

	Babcock	Walther	
		Primary	Secondary
Hydrocarbons	2.1	125	125
Particulates	107	21.5	37.3
NO_x	77.9	22.4	22.4
SO_x	28.1	15.3	21.5
CO	1	1	1

Recognizing that it is completely unscientific and potentially subject to substantial criticism it is proposed to take arithmetic averages of the above values and round them to the nearest multiple of ten to establish a rating basis as follows:

	Average	Rounded
Hydrocarbons	84.0	80
Particulates	55.3	60
NO_x	40.9	40
SO_x	21.6	20
CO	1	1

Table 2. Weighted Emission Rates

Chemical____________________

Process____________________

Increased Capacity______________

Pollutant	Emissions, Lbs./Lb.	Increased Emissions Lbs./Year	Weighting Factors	Weighted Emissions Lbs./Year
Hydrocarbons			80	
Particulates			60	
NO_x			40	
SO_x			20	
CO			1	
			Total	

Increased Emissions (Weighted) by 1980 (continued)

This ranking can be defended qualitatively, if not quantitatively for the following reasons:

1. The level of noxiousness follows the same sequence as is obtained using national air quality standards.
2. Approximately two orders of magnitude exist between top and bottom rankings.
3. Hydrocarbons should probably have a lower value than in the Walther analysis because such relatively non-noxious compounds as ethane and propane will be included.
4. Hydrocarbons should probably have a higher value than in the Babcock analysis because such noxious (or posionous) substances as aromatics, chlorinated hydrocarbons, phenol, formaldehyde, and cyanides are included.
5. Particulates should probably have a higher value than in the Walther analysis because national air standards are based mostly on fly ash while emissions from the petrochemical industry are more noxious being such things as carbon black, phthalic anhydride, PVC dust, active catalysts, etc.
6. NO_x should probably have a higher value than in the Walther analysis because its role in oxidant synthesis has been neglected. This is demonstrated in Babcock's analysis.

Briefly, the procedure, using the recommended factors and Table 2, is as follows:

1. Determine the emission rate for each major pollutant category in terms of pounds of pollutant per pound of final product. This determination is to be made on the basis of data reported on returned questionnaires.
2. Multiply these emission rates by the estimate of increased production capacity to be installed by 1980 (as calculated while determining the number of new plants), to determine the estimated pounds of new emissions of each pollutant.
3. Multiply the pounds of new emissions of each pollutant by its weighting factor to determine a weighted pounds of new emissions for each pollutant.
4. Total the weighted pounds of new emissions for all pollutants to obtain an estimate of the significance of emission from the process being evaluated. It is proposed that this total be named "Significant Emission Index" and abbreviated "SEI".

It should be pointed out that the concepts outlined above are not completely original and considerable credit should be given to Mr. L. B. Evans of the EPA for setting up the formats of these evaluating procedures.

Increased Emissions (Weighted) by 1980 (continued)

(1) Babcock, L. F., "A Combined Pollution Index for Measurement of Total Air Pollution," JAPCA, October, 1970; Vol. 20, No. 10; pp 653-659

(2) Walther, E. G., "A Rating of the Major Air Pollutants and Their Sources by Effect", JAPCA, May, 1972; Vol. 22, No. 5; pp 352-355

Appendix V
Efficiency of Pollution Control Devices

Incinerators and Flares

The burning process is unique among the various techniques for reducing air pollution in that it does not remove the noxious substance but changes it to a different and hopefully less noxious form. It can be, and usually is, a very efficient process when applied to hydrocarbons, because when burned completely the only products of combustion are carbon dioxide and water. However, if the combustion is incomplete a wide range of additional products such as cracked hydrocarbons, soot and carbon monoxide might be formed. The problem is further complicated if the hydrocarbon that is being burned is halogenated, contains sulfur or is mixed with hydrogen sulfide, because hydrogen chloride and/or sulfur oxides then become products of combustion. In addition, if nitrogen is present, either as air or nitrogenated hydrocarbons, oxides of nitrogen might be formed, depending upon flame temperature and residence time.

Consequently, the definition of efficiency of a burner, as a pollution control device, is difficult. The usual definition of percentage removal of the noxious substance in the feed to the device is inappropriate, because with this definition, a "smoky" flare would achieve the same nearly 100 percent rating, as a "smokeless" one because most of the feed hydrocarbon will have either cracked or burned in the flame. On the other hand, any system that rates efficiency by considering only the total quantity of pollutant in both the feed to and the effluent from the device would be meaningless. For example, the complete combustion of one pound of hydrogen sulfide results in the production of nearly two pounds of sulfur dioxide, or the incomplete combustion of one pound of ethane could result in the production of nearly two pounds of carbon monoxide.

For these reasons, it is proposed that two separate efficiency rating be applied to incineration devices. The first of these is a "Completeness of Combustion Rating" and the other is a "Significance of Emission Reduction Rating", as follows:

1. Completeness of Combustion Rating (CCR)

This rating is based on oxygen rather than on pollutants and is the pounds of oxygen that react with the pollutants in the feed to the device, divided by the theoretical maximum number of pounds that would react: Thus a smokeless flare would receive a 100 percent rating while a smoky one would be rated somewhat less, depending upon how incomplete the combustion.

In utilizing this rating, it is clear that carbon dioxide and water are the products of complete combustion of hydrocarbons. However, some question could occur as to the theoretical completion of combustion when burning materials other than hydrocarbons. It is recommended that the formation of HX be considered complete combustion of halogenated hydrocarbons since the oxidation most typically does not change the valence of the halogen. On the other hand, since some incinerators will be catalytic in nature it is recommended that sulfur trioxide be considered as complete oxidation of sulfur bearing compounds.

Efficiency of Pollution Control Devices

1. Completeness of Combustion Rating (CCR) (continued)

Nitrogen is more complex, because of the equilibria that exist between oxygen, nitrogen, nitric oxide, nitrogen dioxide and the various nitrogen radicals such as nitrile. In fact, many scientists continue to dispute the role of fuel nitrogen versus ambient nitrogen in the production of NO_x. In order to make the CCR a meaningful rating for the incineration of nitrogenous wastes it is recommended that complete combustion be defined as the production of N_2, thus assuming that all NO_x formed comes from the air rather than the fuel, and that no oxygen is consumed by the nitrogen in the waste material. Hence, the CCR becomes a measure of how completely the hydrocarbon content is burned, while any NO_x produced (regardless of its source) will be rated by the SERR as described below.

2. Significance of Emission Reduction Rating (SERR)

This rating is based primarily on the weighting factors that were proposed above. All air pollutants in the feed to the device and all in the effluents from the device are multiplied by the appropriate factor. The total weighted pollutants in and out are then used in the conventional manner of calculating efficiency of pollutant removal, that is pollutants in minus pollutants out, divided by pollutants in, gives the efficiency of removal on a significance of emission basis.

Several examples will serve to illustrate these rating factors. as follows:

Example 1 - One hundred pounds of ethylene per unit time is burned in a flare, in accordance with the following reaction:

$$3C_2H_4 + 7\ O_2 \longrightarrow C + 2\ CO + 3\ CO_2 + 6\ H_2O$$

Thus, 14.2 lbs. of particulate carbon and 66.5 lbs. of carbon monoxide are emitted, and 265 lbs. of oxygen are consumed.

Theoretical complete combustion would consume 342 lbs. of oxygen in accordance with the following reaction:

$$C_2H_4 + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O$$

Thus, this device would have a CCR of 265/342 or 77.5%

Assuming that one pound of nitric oxide is formed in the reaction as a result of the air used for combustion (this is about equivalent to 100 ppm), a SERR can also be calculated. It should be noted that the formation of this NO is not considered in calculating a CCR because it came from nitrogen in the air rather than nitrogen in the pollutant being incinerated. The calculation follows:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

Pollutant	Weighting Factor	Pounds in		Pounds out	
		Actual	Weighted	Actual	Weighted
Hydrocarbons	80	100	8000	0	
Particulates	60	0		14.2	852
NO_x	40	0		1	40
SO_x	20	0		0	
CO	1	0		66.5	66.5
Total			8000		958.5

$$SERR = \frac{8000 - 958.5}{8000} \times 100 = 88\%$$

Example 2 - The same as Example 1, except the hydrocarbons are burned to completion. Then,

$$CCR = \frac{342}{342} \times 100 = 100\%$$

and

$$SERR = \frac{8000 - 40}{8000} = 99.5\%$$

Example 3 - One hundred pounds per unit time of methyl chloride is incinerated, in accordance with the following reaction.

$$2\ CH_3Cl + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O + 2\ HCl$$

This is complete combustion, by definition, therefore, the CCR is 100%. However, (assuming no oxides of nitrogen are formed), the SERR is less than 100% because 72.5 lbs. of HCl are formed. Hence, considering HCl as an aerosol or particulate;

$$SERR = \frac{100 \times 80 - 72.5 \times 60}{100 \times 80} \times 100 = 45.5\%$$

The conclusion from this final example, of course, is that it is an excellent combustion device but a very poor pollution control device, unless it is followed by an efficient scrubber for HCl removal.

Example 4 - The stacks of two hydrogen cyanide incinerators, each burning 100 pounds per unit time of HCN are sampled. Neither has any carbon monoxide or particulate in the effluent. However, the first is producing one pound of NO_x and the second is producing ten pounds of NO_x in the same unit time. The assumed reactions are:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

$$4\ HCN + 5\ O_2 \longrightarrow 2\ H_2O + 4\ CO_2 + 2\ N_2$$

$$N_2\ (\text{atmospheric}) + XO_2 \longrightarrow 2\ NO_x$$

Thus, $CCR_1 = 100\%$ and $CCR_2 = 100\%$ both by definition.

However, $SERR_1 = \dfrac{100 \times 80 - 1 \times 40}{100 \times 80} \times 100 = 99.5\%$

and $SERR_2 = \dfrac{100 \times 80 - 10 \times 40}{100 \times 80} \times 100 = 95\%$

Obviously, if either of these were "smoky" then both the CCR and the SERR would be lower, as in Example 1.

Other Pollution Control Devices

Most pollution control devices, such as bag filters, electrostatic precipitators and scrubbers are designed to physically remove one or more noxious substances from the stream being vented. Typically, the efficiency of these devices is rated relative only to the substance which they are designed to remove and for this reason could be misleading. For example:

1. The electrostatic precipitator on a power house stack might be 99% efficient relative to particulates, but will remove little or none of the SO_x and NO_x which are usually present.

2. A bag filter on a carbon black plant will remove 99 + % of the particulate but will remove none of the CO and only relatively small amounts of the compounds of sulfur that are present.

3. A water scrubber on a vinyl chloride monomer plant will remove all of the hydrogen chloride but only relatively small amounts of the chlorinated hydrocarbons present.

4. An organic liquid scrubber on an ethylene dichloride plant will remove nearly all of the EDC but will introduce another pollutant into the air due to its own vapor pressure.

For these reasons, it is suggested again that two efficiency ratings be applied. However, in this case, the first is merely a specific efficiency as is typically reported, i.e., "specific to the pollutant (or pollutants) for which it was designed", thus:

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

The second rating proposed is an SERR, defined exactly as in the case of incinerators.

Two examples will illustrate these ratings.

Efficiency of Pollution Control Devices

Other Pollution Control Devices (continued)

Example 1 - Assume that a catalytic cracker regenerator effluent contains 100 pounds of catalyst dust, 200 lbs. of carbon monoxide and 10 pounds of sulfur oxides per unit time. It is passed through a cyclone separator where 95 pounds of catalyst are removed. Therefore,

$$SE = \frac{100 - 5}{100} \times 95\%$$

and $$SERR = \frac{(100 \times 60 + 10 \times 20 + 200 \times 1) - (5 \times 60 + 10 \times 20 + 200 \times 1)}{(100 \times 60 + 10 \times 20 + 200 \times 1)} \times 100$$

$$= \frac{6400 - 700}{6400} \times 100 = 89\%$$

Example 2 - Assume that an organic liquid scrubber is used to wash a stream containing 50 pounds of SO_2 per unit time. All but one pound of the SO_2 is removed but two pounds of the hydrocarbon evaporate into the vented stream. Then

$$SE = \frac{50 - 1}{50} \times 100 = 98\%$$

and $$SERR = \frac{(50 \times 20) - (1 \times 20 + 2 \times 80)}{(50 \times 20)} \times 100$$

$$= \frac{1000 - 180}{1000} \times 100 = 82\%$$